

NEA NUCLEAR SCIENCE COMMITTEE

ACTINIDE SEPARATION CHEMISTRY IN NUCLEAR WASTE STREAMS AND MATERIALS

December 1997

**NUCLEAR ENERGY AGENCY
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT**

FOREWORD

The separation of actinide elements from various waste materials is a significant problem facing developed countries. The issue arises primarily because of the potential long-term hazard of many of the actinides, but is also due to the regulatory requirements associated with actinide waste disposal, which are different from those associated with other radioactive wastes. The different regulations are in turn related to the different health hazards and generally longer half lives of the actinides. This issue is of continuing interest to the OECD/NEA Member countries primarily in relation to waste produced within power station fuel recycle. Similar problems exist for waste produced in the past as a result of nuclear weapons production programmes and wastes likely to be produced in the future emerging from operations required for waste disposal.

The Nuclear Science Committee, representing the interests of the basic R&D in the OECD/NEA Member countries, has established a task force of experts in actinide chemistry to review the current and developing separation techniques and chemical processes of interest in separating actinides. This task force was commissioned with the preparation of a report on the subject. The task force members are listed in Annex 1.

This report is intended to provide a timely and representative guide to technical journals and other sources of separation chemistry information on the actinide elements. An important objective is to provide information that may be used to conserve energy and protect humans and the environment.

The areas discussed include sources, types and amounts of actinide wastes and their relative importance; availability of basic actinide separation chemistry information; existing effective, efficient and economical waste stream processes for actinides; actinide separation processes developed or undergoing development; and the needs for additional basic actinide separation chemistry data. In addition, an attempt is made to prioritise needs for additional separation development work and to make recommendations using a 25 year horizon for those needs as a practical extension into the future.

For related material see <http://www.nea.fr/html/science/chemistry/>

The opinions expressed in this report are those of the authors only and do not necessarily represent the position of any Member country or international organisation. This report is published on the responsibility of the Secretary-General of the OECD.

Acknowledgement

The authors wish to acknowledge Professors Jan-Olov Liljenzin of Goteborg, Sweden, Gregory Choppin of Tallahassee, Florida, and Robert Guillaumont of IPN, France for their critical reviews and excellent suggestions for improvements to this report.

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EXECUTIVE SUMMARY

The separation of actinide elements from various waste materials, produced either in nuclear fuel cycles or in past nuclear weapons production, represents a significant issue facing developed countries. Improvements in the efficiencies of the separation processes can be expected to occur as a result of better knowledge of the chemistry of the elements in these complex matrices. The Nuclear Science Committee of the OECD/NEA has established a task force of experts in actinide separation chemistry to review current and developing separation techniques and chemical processes.

The report consists of eight chapters. In Chapter 1 the importance of actinide separation chemistry in the fields of waste management and its background are summarised. In Chapter 2 the types of waste streams are classified according to their relative importance, by physical form and by source of actinides. The basic data of actinide chemical thermodynamics, such as oxidation states, hydrolysis, complexation, sorption, Gibbs energies of formation, and volatility, were collected and are presented in Chapter 3. Actinide analyses related to separation processes are also mentioned in this chapter. The state of the art of actinide separation chemistry is classified in three groups, including hydrometallurgy, pyrochemical process and process based on fields, and is described in Chapter 4 along with the relationship of kinetics to separations. In Chapter 5 basic chemistry research needs and the inherent limitation on separation processes are discussed. Prioritisation of research and development is discussed in Chapter 6 in the context of several attributes of waste management problems. These attributes include: 1) mass or volume of the waste; 2) concentration of the actinide in the waste; 3) expected difficulty of treating the wastes; 4) short-term hazard of the waste; 5) long-term hazard of the waste; 6) projected cost of treatment; 7) amount of secondary waste.

Based on the priority, recommendations were made for the direction of future research activities in actinide separation chemistry from view points of basic chemical data and separation chemistry, as shown in Chapter 7.

Section 1
INTRODUCTION

The separation of actinide elements from various waste materials is a significant problem facing developed countries. The issue arises primarily because the regulatory requirements associated with actinide waste disposal are different from those associated with other radioactive wastes. The different regulations in turn are related to the various health hazards and generally longer half lives of the actinides. This issue is of continuing interest to the OECD/NEA Member countries primarily in relation to waste produced within power station fuel recycle. Similar problems exist for waste produced in the past as a result of nuclear weapons production programmes and wastes likely to be produced in the future emerging from operations required for waste disposal.

The chemical behaviour of actinides is complex, and it is necessary to understand it more fully to be able to optimise separation processes under various conditions, as well as processes related to environmental clean-up.

1.1 Relationship of the Task Force on Actinide Separation Chemistry to the NEA and the NSC

The Nuclear Science Committee, representing the interests of the basic R&D in its Member countries, has established a task force of experts in actinide chemistry to review current and developing separation techniques and chemical processes of interest in separating actinides, and to prepare a report on this subject.

This report includes a detailed assessment of these techniques and processes, and concludes with a number of recommendations for future research and development. Research organisations in Member countries can draw on this international consensus on the state of the art in actinide separation chemistry to help orient their programmes most effectively.

1.2 Importance of the report to waste management

Management of radioactive wastes is an important issue for technical, social and political reasons. The so-called “legacy wastes” from nuclear weapons production, nuclear fuel reprocessing wastes, medical and industrial isotope production wastes and spent fuel designated as waste by some countries pose current and pressing problems. In addition, significant amounts of uranium and thorium exist in some residues from uranium and rare earth ore processing, and although these are not usually considered in the same context as other radioactive wastes, they are nonetheless wastes. All of these wastes must be safely managed and disposed of. This report presents separation processes of present and potential usefulness in waste management.

1.3 Importance of the report to Member countries

Although not all of these waste management problems exist in each of the OECD/NEA Member countries, it is clear that the countries are dealing with at least one or more of the problems listed. Actinide elements comprise a major class of wastes, and wastes containing actinides are considered the most difficult and troublesome because the elements are radiotoxic, and many have long half lives.

As requirements change and additional types and sources of wastes are identified, new technologies are developed to meet new needs and to provide less costly ways of managing wastes. It is important to provide timely information to the OECD Member countries so they may take advantage of new developments as they occur, many of which are reported through the normal technical publication channels many months or even years after they are first tested and successfully implemented.

1.4 International waste stream treatment activities

Treatment of radioactive waste streams is receiving considerable attention in most countries containing nuclear power plants, particularly those that either have or have had operated nuclear fuel reprocessing plants. In the US, for example, most of the wastes are a legacy from the US Department of Energy (US DOE) nuclear weapons production, although there is some reprocessing waste from the small, inactive Nuclear Fuel Services reprocessing plant in West Valley, New York. Other countries such as France, the United Kingdom, Russia, Japan, China and India have ongoing reprocessing activities that produce radioactive waste. Because radioactive wastes are a continuing, unresolved problem, and because there is little economical incentive for competition among nations in radioactive waste disposal, there is international collaboration in studies of waste management and disposal.

There are frequent international meetings on all aspects of waste disposal in areas ranging from separation chemistry and technology to transport of radionuclides through the biosphere and from geological repositories for wastes. France developed the SPIN programme and Japan the very similar OMEGA programme to study the separation and transmutation of actinides into fission products and to attempt the further transformation of long-lived fission products into stable isotopes. Russia is studying the recycle of fissile elements to reactors as a way of producing power. In the United States a study by the National Academy of Sciences [1] concluded that there was neither sufficient economic nor safety incentives to proceed with transmutations at this time. There are information and personnel exchange programmes among many nations such as France and the US, Russia and the US, and Germany and China (in the area of waste vitrification). In addition, closely related research is pursued collaboratively among many nations in universities around the world.

1.5 Nature of waste streams

In terms of potential health significance for the far distant future, the actinides in intact fuel or high-level reprocessing waste greatly outweigh those from all other α -emitting sources. Of more immediate concern is the amount in liquid wastes discharged from fuel reprocessing plants, as witness the efforts made to reduce α -active discharges over the past twenty years. The low-level waste stored in near-surface repositories are of intermediate concern. (In a practical sense, however, none is likely to be as important a source of radiation as the uranium and thorium and their decay products naturally present in all rocks and soils.)

Table 1.1 highlights the relationship of the actinide elements to lanthanide elements. In general, the lower-atomic-number actinides are the ones of interest in waste stream clean-up. Not only are the elements above curium present in low concentration in waste streams, but also most of them can only be made under highly specialised conditions. A crude indication of the chemical nature of the actinides may be inferred from corresponding lanthanide elements. The chemistry of a trivalent transplutonium element directly under each lanthanide element (and of uranium and plutonium in their trivalent states) is similar to that of the lanthanide element. This correlation holds especially well for elements that occur later in the series. For example, the chemistry of americium(III) is similar to that of europium(III).

Table 1.1. Periodic relationship of actinides to lanthanides

Lanthanide Series	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinide Series	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

Table 1.2 lists the α -emitters important in waste stream treatment. Radium and radon are included because they are present in many actinide wastes as radioactive decay daughters of actinides, and because they can constitute a significant hazard.

Table 1.2. α -emitters important in waste stream treatment

Actinide isotope	Atomic no.	Half life
Uranium-232	92	69.80 y
Uranium-233		1.59E+05 y
Uranium-234		2.46E+05 y
Uranium-235		7.04E+08 y
Uranium-238		4.47E+09 y
Neptunium-237	93	2.14E+06 y
Plutonium-238	94	87.70 y
Plutonium-239		2.41E+04 y
Plutonium-240		6.56E+03 y
Plutonium-242		3.74E+05 y
Americium-241	95	4432.70 y
Americium-242m		141.00 y
Americium-243		7.36E+03 y
Curium-243	96	30.00 y
Curium-244		18.10 y
Curium-245		8.50E+03 y
Curium-246		4.73E+03 y
Thorium-230	90	7.54E+04 y
Thorium-232		1.40E+10 y
Radium-226	88	1.60E+03 y
Radon-222	86	3.83 d

* Reference: JEF-2.2 Radioactive Decay Data, OECD/NEA, JEF Report 13, August 1994

1.6 Management schemes

Waste management schemes differ from country to country, but the philosophical approach adopted in nearly all countries is to dispose of these wastes in environmentally acceptable ways that minimise production of additional large volumes of low-level wastes. Although the guidelines established for managing radioactive wastes are quite similar in most countries, a continuing impediment to implementation of these guidelines and regulations are constantly changing, almost always in a direction requiring more complete and more difficult chemical separations.

1.7 Reduction in amounts of wastes discharged into the environment

There is a strong international commitment toward reducing the discharge of wastes into the environment. In the early days of the nuclear era it was widely believed that a “dilute and disperse” approach to waste management was valid, especially for relatively small amounts of waste. The rationale for this approach was that if the low-level wastes were homogeneously mixed with the earth’s crust and the oceans, their concentrations would be so low that they would be innocuous, if not actually almost undetectable. In more recent years it has become apparent that natural processes, especially biological processes, tend to concentrate many of the radioactive elements discharged. For this reason, and in the interests of a more conservative approach to radioactive management, it is becoming increasingly unacceptable to discharge retainable wastes to the environment.

It remains to be seen what the eventual impact will be of the adoption of regulations that permit the use of radioactively contaminated materials in commerce (materials containing radioactivity below the so-called “*de minimus*” levels). Clearly there will be some residual radiation, but if the “*de minimus*” radiation level of a material is so low as to pose essentially no threat to health or safety it may be found to be acceptable for release to the general public.

1.8 Scope and objectives

This report is intended to provide a timely and representative guide to technical journals and other sources of separation chemistry information on the actinide elements. An important objective is to provide information that may be used to conserve energy and protect both humans and the environment.

The areas discussed include sources, types and amounts of actinide wastes and their relative importance; availability of basic actinide separation chemistry information; existing effective, efficient and economical waste stream processes for actinides; actinide separation processes developed or undergoing development; and the need for additional basic actinide separation chemistry data. In addition, an attempt is made to prioritise the needs for additional separation development work and to make recommendations using a 25 year horizon for those needs as a practical extension into the future.

Section 2

TYPES OF WASTE STREAMS

2.1 Reasons for importance

The actinide of primary importance in the nuclear industry is uranium. Thorium holds promise of being important in the future. Processes of transmutation and decay in a uranium-fuelled power reactor generate large amounts of neptunium, plutonium, americium and curium and significantly lesser amounts of berkelium and californium. Similar processes in thorium lead to protactinium and ^{233}U . Irradiation of thorium produces little of the transuranium elements, and for that reason it has been proposed as a fuel for actinide burners, particularly those driven by particle accelerators.

If discharged fuel is disposed of directly to a repository all the actinides, including the uranium, remain in it together with the fission products and actinide decay products, until the eventual failure of both cladding and containment allows gradual leaching by ground water. If the fuel is reprocessed, most of the uranium and plutonium are separated; the “minor actinides” are left in the waste, together with the fission products plus, typically, some parts per thousand of the plutonium and some of the uranium. When this mixture is solidified and placed in a repository, many of the same considerations with regard to release of radioactivity will apply as those that apply to the intact fuel.

All the actinides can undergo neutron fission, directly or by way of transmutation products, thus releasing potentially valuable energy as well as reducing the inventory of long-lived waste products. This combination of benefits has been suggested as a justification of the difficulty, expense, additional waste generation and increased operational risks of separating actinides from fission products. While by no means universally accepted (see the discussion above about the National Academy of Sciences study in the US), the approach is being given serious consideration by the Japanese OMEGA programme [2] and the French SPIN programme [3].

Besides present and future wastes from the civil nuclear industry, there remain large volumes of wastes from the early military plutonium production programmes. The management of these wastes could be simplified if the actinides were separated into a small volume. A substantial effort has therefore been directed to this end. The extent to which its results may be applicable to commercial high-level waste will depend on many factors, including risk reduction, cost and social acceptance.

Small amounts of actinides have been used in specific applications such as smoke detection, neutron radiography or activation analysis, and isotopic heat generation sources for thermoelectric generators (heart pacemakers, remote telemetry stations, etc.). Here the separation has already taken place, and the remaining waste management problems are those of retrieval and disposal at the end of service, particularly when the actinides have passed outside of regulatory control. Where installed in launched space vehicles, they may for the most part be beyond practicable means of retrieval.

2.1.1 Hazards, limits

The treatment, storage and transport of actinides as a result of activities in the nuclear fuel cycle may lead to radiological impacts incurred by both the work force and the general population. Because most actinides are α -emitters, the most important exposure pathways associated with actinides are those which result in the uptake of these radionuclides in the human body. With respect to both the workers and the general population, radiation protection principles are applied to minimise the probability of uptake into the body (i.e. the probability of exposure) and the amount of material taken up (i.e. the magnitude of exposure).

Exposure of workers is primarily a result of inhalation or ingestion of actinides present in the work area. Additional exposures may be incurred as a result of uptake through cuts in the skin. The International Commission on Radiological Protection (ICRP) has recommended an annual individual dose limit of 20 mSv (one sievert equals one joule per kilogram) as occupational exposure for radiological workers. The annual dose limit can then be used to derive nuclide-specific secondary limits such as derived air concentration (DAC) and annual limit on intake (ALI). Due to the high radiotoxicity of most actinides, the secondary limits for these radionuclides are generally low.

Exposure of the general population is a result of releases of actinides into the environment. For most stages in the fuel cycle these releases occur in the atmosphere or in surface water. For deep geological repositories such as those proposed for high-level radioactive wastes, such releases would be to the groundwater. The primary exposure pathways are the inhalation of particulate radioactive material present in the air and the ingestion of material which has entered the food chain. The chemical behaviour of the different actinides is an important factor in determining the movement of radionuclides through the environment. The ICRP has recommended an annual individual dose limit of 1 mSv (excluding natural background and medical exposure) for members of the general population.

2.1.2 Quantities

There are very large amounts of radioactive materials stored both as spent fuel and as wastes from fuel reprocessing. The spent fuel is generally stored either in pools of water or in dry storage casks. By far the largest amount of radioactivity stored is in the spent fuel. However, the waste stored in tanks poses the greatest potential hazard. Many of the waste storage tanks, particularly in the US, are well beyond their design lives, and many of them are leaking or are suspected of leaking. In the following, some of the major features of the stored spent fuel and the tank wastes are summarised.

2.1.2.1 Fuel

Most countries with nuclear power plants either reprocess their own fuel or have it reprocessed on a contractual basis. Consequently, large amounts of spent fuel are not accumulating in those countries. In the US however the spent fuel is accumulating in water storage pools at the reactor sites or in central spent fuel storage facilities. Table 2.1 summarises the status of the spent nuclear fuel inventory situation in the US.

The US DOE spent fuel category includes an extremely wide variety of fuels, ranging from the typical highly enriched uranium in aluminium plates to one-of-a-kind experimental fuels, and from metal-to-ceramic-to-carbon compositions.

Table 2.1. US spent nuclear fuel inventory
(taken in part from Table 0.3, p. 15, DOE/RW-0006, Rev. 10, Dec. 1994)

Waste category	Mass, MTIHM ^d	%	Volume, m ³	Activity, EBq ^a	Thermal power, kW
Commercial					
BWRs	10 178	36.3%	4 103 ^b	273	27 200
PWRs	17 851	63.7%	7 196 ^b	751	77 700
US DOE ^c	2 675				
Hanford	2 137	79.9%			
INEL	286	10.7%			
SRS	201	7.5%			
Other	51	1.9%			

^a Calculated as of 31 December 1993 (1 EBq = 27 MCi).

^b Includes volume of spacing between the fuel rods in the assembly.

^c Taken from "DOE Spent Nuclear Fuel Technology Integration Plan", SNF-PP-FS-002, Rev. 0, Figure 3-1, p. 3-7, December 1994.

^d MTIHM: Metric tons initial heavy metal.

2.1.2.2 Tank wastes

Nearly all countries that make any significant use of radioactive materials have some wastes stored in tanks as solutions, sludges, or slurries. In the following sections an attempt is made to give some insight into the magnitude of this problem. This is done by illustrative examples using the tank wastes in the US. These examples were chosen because the US has major amounts of tank waste, and their wastes are representative of the extremes in waste types.

In general, tank wastes are either acidic or alkaline, depending on whether the high-level waste raffinate from solvent extraction or the high-level waste from some other separation process was neutralised with caustic or stored without neutralisation. Separation of actinides from acidic wastes is potentially much simpler than from neutralised wastes. This follows from the fact that actinides precipitate from alkaline media, and in some cases form colloids. For chemical separations to be effective the actinides must be solubilised, and in general, must be put into a separable ionic form.

2.1.2.2.1 Hanford

Some of the largest tank waste volumes are stored on the US DOE's Hanford reservation. Hanford's tanks are cylindrical structures of reinforced concrete with inner carbon steel liners. The tanks are of two basically different designs: 149 have only a single carbon steel liner, and 28 have two steel liners separated by an annular space. The tanks are referred to as the single-shell tanks (SSTs) and the double-shell tanks (DSTs), respectively. The SSTs have domes of concrete without a steel liner. The DSTs are completely enclosed by steel and reinforced by a concrete shell. Both types of tank are covered with about 10 feet (~3 m) of soil and gravel. The SSTs were built in four sizes ranging from 55 000 gallons to 1 million gallons (208 to 3 785 m³). The DSTs all have capacities of 1.1 to 1.2 million gallons (4 164 to 4 542 m³).

Hanford tank waste data is based primarily on historical records of transfers and is not reliable on a tank-by-tank basis. However, the overall inventory of tank wastes is considered to be more accurate. The major features of the Hanford tank wastes were established when the acidic liquid

wastes produced by reprocessing spent fuel to recover plutonium were neutralised with sodium hydroxide. This action produced precipitates which have hardened over time in some of the tanks. Repeated evaporation to reduce the waste volume has resulted in saturated solutions and the concomitant precipitation of the salts produced by neutralisation. Table 2.2 shows the actinide content of Hanford tanks. The estimated total masses of sludge, saltcake, and interstitial liquid in the tanks are given in Table 2.3, and Table 2.4 presents the tanks' total radioactivity content.

Table 2.2. Actinide content of Hanford tanks [4]

Attribute	Double-shell tanks	Single-shell tanks
Volume, m ³	7.8×10 ⁴	1.4×10 ⁵
Density, kg/m ³	approx. 1 500	approx. 1 600
Mass, tonnes	1.2×10 ⁵	2.2×10 ⁵
Nuclide	Total actinide radioactivity, PBq*	
²³⁵ U	2.6×10 ⁻⁶	7.4×10 ⁻⁴
²³⁸ U	2.4×10 ⁻⁵	1.7×10 ⁻²
²³⁷ Np	1.1×10 ⁻³	1.2×10 ⁻³
²³⁸ Pu	1.6×10 ⁻²	1.6×10 ⁻²
²³⁹ Pu	0.34	0.81
²⁴⁰ Pu	9.6×10 ⁻²	0.20
²⁴¹ Pu	0.19	1.7
²⁴¹ Am	3.7	1.7
²⁴³ Am	----	7.0×10 ⁻³
²⁴⁴ Cm	5.6×10 ⁻²	2.6×10 ⁻³
Total radioactivity	4.37	3.69
Element	Total actinides, kg	
Uranium	3.6×10 ⁴	1.4×10 ⁶
Neptunium	4.2×10 ¹	4.6×10 ¹
Plutonium	1.6×10 ²	3.8×10 ²
Americium	2.9×10 ¹	1.4×10 ¹
Curium	1.9×10 ⁻²	8.6×10 ⁻⁴

* 1 PBq = 27 000 curies

Table 2.3. Non-radioactive contents of Hanford tanks

Estimated masses of non-radioactive chemical components in SST and DST waste, tonnes							
Single-shell tanks				Double-shell tanks			Overall SSTs and DSTs
Sludge	Saltcake	Interstitial liquid	Total	Soluble	Insoluble	Total	
75 500	137 000	11 600	224 000	131 000	1 450	133 000	357 000

The estimated total radionuclide inventories for the SSTs and DSTs are given in the following table.

Table 2.4. Radioactivity content of Hanford waste tanks

Estimated radionuclide inventories for SSTs and DSTs, EBq*			
SSTs total	DSTs		
	Soluble	Insoluble	Total
3.85	1.94	0.755	2.69

* Radionuclide amounts are calculated to include decay and growth to 31 December 1999 (1 EBq = 27 MCi).

From these tables it may be seen that both the mass of Hanford tank waste and its radioactivity content are very large.

2.2 By physical form

Table 2.5 shows the physical forms in which the various wastes are present.

Table 2.5. Physical forms of wastes

Solids	Liquids	Sludges	Colloids
Mine/mill tailings	Process waste water	Used drilling mud	Ground-water percolate
Process residues	Pond water		
Fluoride conversion residues			
Cladding hulls		Corroded cladding	
Spent ion exchangers	Regenerants		
Insoluble fission products	Condensates	Flocculation precipitates	Flocculation supernate
Solidified HLW**	Solvent extraction raffinates	Tank deposits	
Solvent degraded products	Waste solvent	Cruds	
Unprocessed fuels	Solvent washings		
Pyrometallurgical residues	Analytical residues		
Filters			
Isotopic heat sources	Decontaminant solutions		
Scrap plant items			
Scrap tools etc.			
Protective clothing			
Cleaning materials			
Office waste			
Structural debris			
Contaminated soil			
Academic & medical wastes			

** HLW: High-level waste. In general HLW denotes waste having high levels of radioactivity. In the US it is formally taken to mean wastes arising from the first solvent extraction cycle during fuel reprocessing.

2.2.1 Solids

The principal actinide-containing waste solids are unprocessed fuel and solidified HLW; heat sources from isotopic thermoelectric generators may be added as they are relatively easy to treat if retrieved from their applications. Where HLW has been solidified for the purpose of final disposal, further treatment would be both difficult and contradictory. Recovery of actinides from fuel is possible only through reprocessing. Under current practices, the minor actinides extracted from waste streams then merges with recovery from solvent-extraction raffinates.

In terms of total waste volume contaminated soils head the list. Such wastes are important because they threaten pollution of water supplies and they impede eventual return of the site to unrestricted public use (sometimes referred to as “green field” status). Part of the radioactive content of soil may be removed by a variety of remediation measures, such as percolating a complexant solution through the soil. The remaining radioactivity could be fixed in place by *in situ* vitrification or by emplacement of barriers. Decontamination is hampered by the quantities and nature of material involved, by some risk of aggravating rather than curing the problem and by the ill-defined physical boundaries of the contaminated soil.

With the other solids listed, the actinide content is relatively slight, and removal if attempted is essentially a matter of decontamination to simplify disposal. This problem then merges with the treatment of decontamination solutions. Actinide chemistry related to the treatment of solids thus becomes one of either complete or partial dissolution or of fixation.

2.2.2 Aqueous solutions

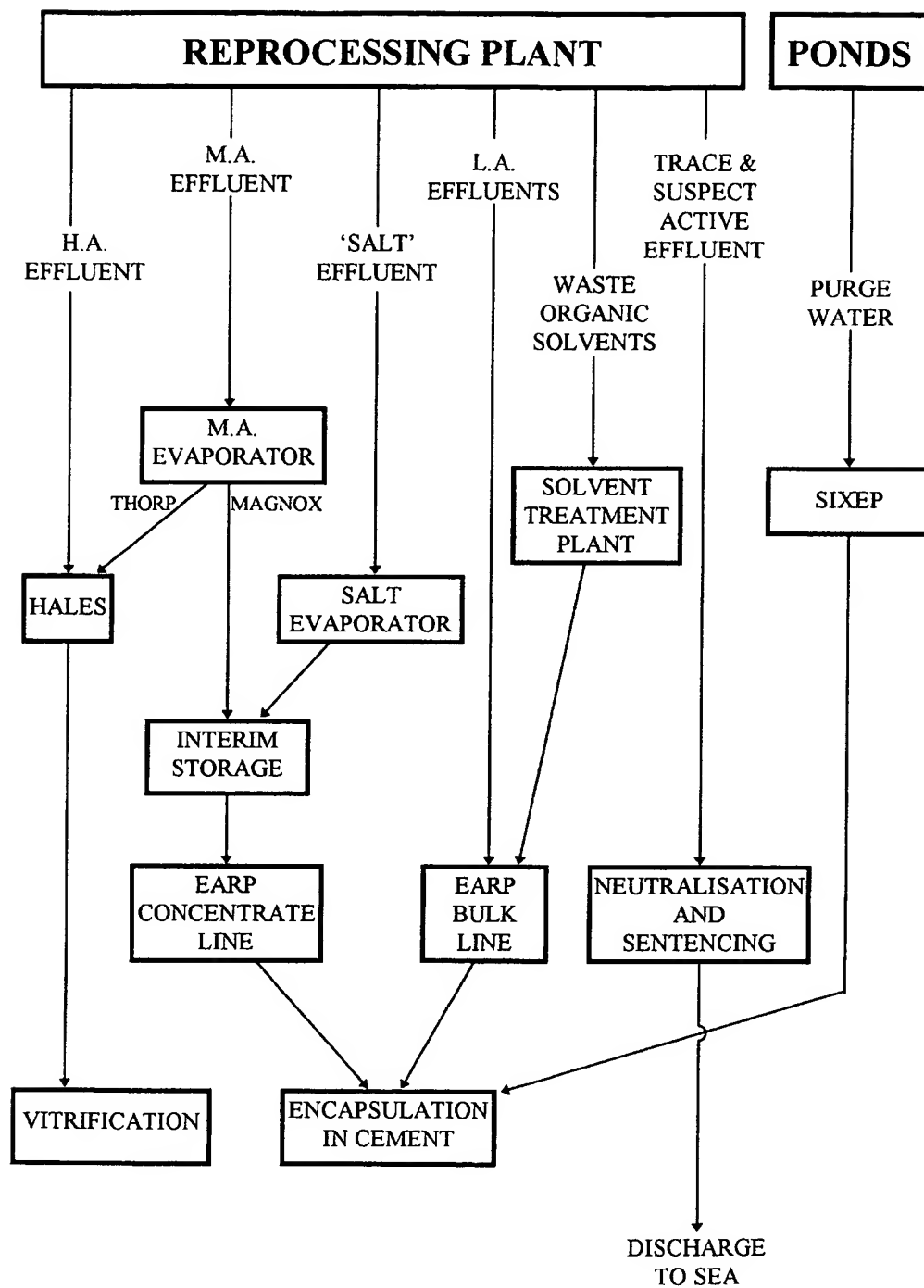
Aqueous solutions may be divided into those of high or low ionic strength, although such a division is somewhat arbitrary in that the terms are relative, and the boundary might be crossed on concentrating or diluting a particular solution. Furthermore, waste solvent that is inherently of low ionic strength may be treated by means that produce a concentrated solution. Thus the effective division is between those liquors that are too dilute for concentration by physical means (such as evaporation) to be economically feasible, and others for which it is actually or potentially practised. As an example of a general strategy of aqueous effluent management, the general scheme at the Sellafield reprocessing site is shown in Figure 2.1. The ion exchange material used in pond-water treatment is often a natural mineral and is disposed of as solid rather than regenerated.

2.2.2.1 High ionic strength

The principal high ionic strength liquid containing minor actinides is the aqueous raffinate from solvent-extraction processing of irradiated nuclear fuel. This is evaporated and fractionated to give a concentrate (stored to allow partial decay of heat-releasing fission products before eventual vitrification), a recovered acid stream recycled to the process and a condensate slightly contaminated by volatilised or entrained radionuclides.

The alkaline solution used for the solvent washing in fuel reprocessing contains small amounts of many α - or β/γ -emitting radionuclides. It may be neutralised and concentrated. Treatment may lead directly or indirectly to the production of solids, sludges or colloids, and a salt solution with too high a sodium content for convenient vitrification.

Figure 2.1 Liquid effluent treatment scheme, Sellafield plant



The solvent used in the solvent extraction process for recovering uranium and plutonium eventually requires disposal. Direct incineration is generally not practicable because of the production of highly corrosive phosphoric acid fume, but it may be possible for the purely organic moiety after pyrolysis or hydrolytic decomposition. Alternatively, distillation may purify a portion of the solvent sufficiently for recycle after adjustment of the composition, but it leaves a higher-boiling residue still needing treatment, as would residues from pyrolysis. An alkaline hydrolysate, containing salts of phosphoric acid and acid esters together with most of the radioactivity, may be decontaminated by flocculation precipitation.

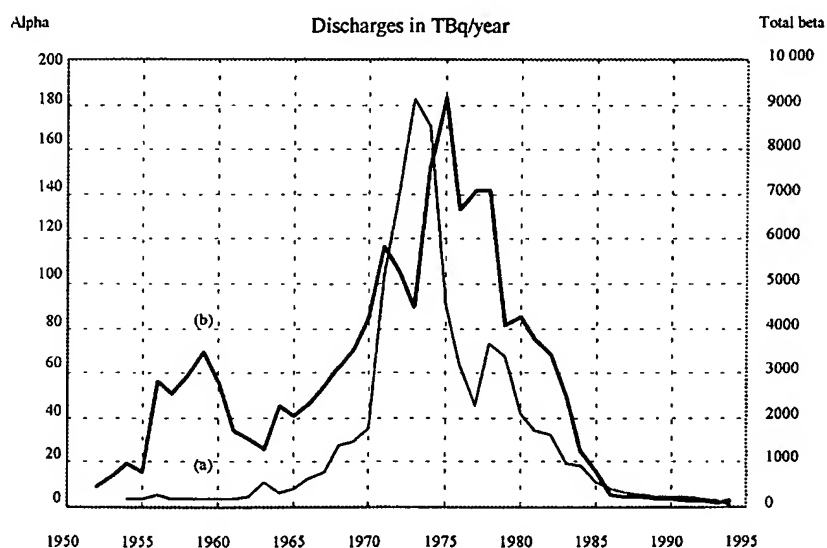
Decontaminant solutions may also be of relatively high ionic strength because of acid content. A simple acid solution could be combined with other streams such as solvent-extraction raffinate. However, decontaminants commonly contain complexing agents designed to solubilise actinides or fission products, and therefore are inherently liable to interfere with subsequent treatment unless they are first destroyed.

Solutions used to regenerate ion exchangers are of necessity high in ionic strength. Their treatment depends on their compositions. If the resins have been used to treat fuel storage pond water, then the actinide levels are usually negligible since the contaminants are predominantly alkali and alkaline earth fission products, together perhaps with activated corrosion products.

2.2.2.2 Low ionic strength

The predominant low ionic strength waste stream is the water discharged from cooling ponds for irradiated fuel. As indicated above, the actinide content is low or negligible. Filtration and ion exchange are commonly employed to reduce the radioactivity enough for discharge to the environment. For example, at Sellafield and La Hague effluent levels have been substantially reduced (as shown in Figure 2.2 for the case of Sellafield). The α -emitting radioisotope discharges are from other areas of the plant.

Figure 2.2 Discharges of (a) α - and (b) β -emitters from the Sellafield plant



2.2.3 Sludges

Sludges from corroded cladding may come from transport casks and handling or storage ponds. Whenever it is convenient they are flushed out and encapsulated for disposal. The same applies to crud formed in processing. Substantial amounts of sludge are formed in the flocculation precipitation of radionuclides, e.g. by hydrolysis of ferric salts. These are de-watered as far as practicable and encapsulated for disposal.

Sludge deposits in tanks, particularly in those where highly-active raffinates have been neutralised, differ in having much higher radioactivity and substantial amounts of additional inactive species such as aluminium hydroxide. For example, the Hanford single shell tanks contain 75 500 tonnes of sludge [5], and the Savannah River tanks contain 3 310 tonnes of sludge [6], the bulk of which is composed of non-radioactive materials. The sludge deposits may be difficult to remove and potentially unsafe to leave in place, so their treatment requires careful consideration.

Mud and rock debris discharged from drilling rigs may also contain enough natural radionuclides to come under regulatory control.

2.2.4 Colloids

The principal concerns about colloids arise in connection with their potential to facilitate movement of radioactivity in the environment and to make separations difficult. The long-term safety of proposed deep geological repositories for radioactive waste depends in part on the tendency of dissolved or suspended species, for instance plutonium, to be absorbed by minerals in the surrounding rock. This absorption may be significantly reduced if the radionuclide itself is in colloidal form or is complexed by colloids of a polyelectrolytic nature, such as are formed by the decay of organic matter. The existence of colloidal actinides may greatly enhance the mobility of the nuclides in question. The tendency of some actinides, notably plutonium, to form colloids increases the likelihood of actinides remaining with the supernatant solutions above the tank sludges and saltcakes, thus jeopardising the classification of the supernatant solutions and their subsequent waste forms as non-TRU, low-level wastes.

2.3 By sources of actinides

Many nuclear industry processing streams contain actinides. They may be divided into the following categories.

2.3.1 Residues from mining, milling and purification

Tailings from milling uranium ore contain significant fractions of the original uranium. The tailings are significant less because of the uranium present than because of the daughter elements which (apart from radon which, being gaseous, may diffuse out) also remain in the residues. When solvents or ion-exchange resins have been used in processing ore or concentrates, the solvents or the resins eventually form an organic waste retaining some fraction of the actinide throughput. In global terms uranium mining and milling represent the major health and environmental hazard of the nuclear industry. Michaels [7] puts the risks associated with various aspects of the nuclear fuel

cycle in perspective. The risks associated with front-end waste management (apart from mining and milling) are relatively very small both on an absolute basis and when compared with the dangers linked to mining and milling and with nuclear power generation.

2.3.2 Residues from conversion and enrichment

Some waste solids and sludges are formed in the front end of the fuel cycle. They typically contain fluorine compounds, principally of uranium (UF_4 and UO_2F_2). Traces of plutonium are also present even with unrecycled material, and are concentrated above the natural proportion. With a recycled feed such contamination is liable to be greater, and other minor actinides may be present. The presence of ^{232}U , even at the parts per million level, causes radiation problems because of the build-up of ^{208}Tl and other daughters in the decay chain.

Where sodium fluoride or other impurity sorbent beds are used for purification of UF_6 they too will eventually become actinide-bearing waste.

2.3.3 Back-end of the fuel cycle

In terms of radioactivity it is the back-end of the fuel cycle where the most serious actinide waste separation problems exist.

2.3.3.1 Discharged nuclear fuel for direct disposal

Spent nuclear fuel contains the entire residual actinide inventory generated during irradiation, but if it is not to be reprocessed, the option of special treatment for the actinides does not arise. There may, however, be concern about their behaviour, particularly in failed fuel elements.

2.3.3.2 High-level waste

Commercial fuel reprocessing waste contains significant amounts of uranium and lesser, although not negligible, amounts of plutonium. As a concrete example, the composition derived from a flowsheet for reprocessing LWR fuel in the UK is given in Table 2.6. An additional point to note is the large amount of lanthanides (nearly 12 g/kg-U of fission product lanthanides in addition to a similar amount of gadolinium added as a neutron poison in this particular flowsheet) which are chemically analogous to the much smaller quantities of higher actinides and tend to accompany them in separation processes.

2.3.3.3 Intermediate-level waste

Fuel cladding fragments and general reprocessing waste, while they do not generate significant amounts of decay heat, are too radioactive for classification as low-level waste. This type of waste includes plutonium-contaminated operating wastes and dissolver residues (undissolved fuel, cladding fines and refractory metals) which may contain appreciable but varying proportions of actinides. Filters contaminated with actinides from failed fuel elements in the once-through scheme may be included in this category.

**Table 2.6. First cycle waste assumed from LWR fuel (UK)
40 kW/kg, 40 MWd/kg, 5-year cooled, in mg/kg-uranium in fuel**

Atomic no.	Element	mg/kg-U	Atomic no.	Element	mg/kg-U
24	Cr	225	52	Te	646
26	Fe	850	55	Cs	2 901
28	Ni	162	56	Ba	2 043
31	Ge	1.46	57	La	1 481
33	As	0.041	58	Ce	2 778
34	Se	66.84	59	Pr	1 414
37	Rb	410	60	Nd	4 997
38	Sr	963	61	Pm	<50
39	Y	529	62	Sm	1 060
40	Zr	4 226	63	Eu	184
42	Mo	4 040	64	Gd	12 193
43	Tc	1 020	65	Tb	4.42
44	Ru	2 878	66	Dy	2.18
45	Rh	525	68	Er	0.10
46	Pd	1 826	92	U	25
47	Ag	36	94	Np	457
48	Cd	115	94	Pu	18
49	In	2.9	95	Am	59
50	Sn	105	96	Cm	33
51	Sb	25.5		PO ₄ ³⁻	75
Volume approx. 0.250 l/kg-uranium processed					

* In addition, there are 4.7 MBq of berkelium-249 and 1 MBq of californium (various isotopes) per tonne of fuel processed. The entire fission yield of technetium, platinum metals, etc. is included although a substantial proportion is liable to remain in dissolver residues which may follow a different disposal route from the rest.

2.3.3.4 Low-level wastes (solid and liquid)

In general low-level wastes (LLW) contain actinides but in traces judged to have insufficient environmental significance to warrant their removal.

2.3.3.5 US military wastes in priority order

- *Alkaline aqueous wastes* are typically neutralised fuel reprocessing wastes with significant amounts of uranium and low concentrations of plutonium, neptunium (americium and Cm). Wastes stored at the US DOE Hanford site are representative of this type of waste.
- *Acidic aqueous wastes* are typically un-neutralised fuel reprocessing wastes with low concentrations of plutonium, neptunium (americium and curium). These wastes, which also may contain substantial amounts of fluoride, zirconium and aluminium are representative of those stored at the US Idaho Falls site.

- *Solid wastes in alkali metal chloride salt matrices* with low concentrations of plutonium and americium are typified by scrap from weapons recycle operations. These wastes are representative of those stored at the US Rocky Flats Environmental Technology Site.
- *Neutral aqueous wastes* are typified by “cribbed” wastes (those wastes dumped into lined trenches in the ground) from fuel reprocessing or heavy metal production and recovery activities. They may be in the presence of natural organic complexants such as humic acids, and have low concentrations of uranium, plutonium, neptunium, americium and curium. These wastes are representative of some of the wastes in the environment at the Hanford, Savannah River and Oak Ridge sites.

The neutral aqueous waste category presents substantial problems with regard to land remediation. Similar considerations no doubt apply to the environment of certain former Soviet establishments where discharge to ground was for some time the accepted disposal route.

Especially in neutral or alkaline solution, actinides are liable to be colloidal or to be associated with solid or colloidal material of other kinds. In this chemical form their behaviour may differ widely from that of their ionic forms, as noted above.

2.3.3.6 Sludges from effluent treatment

Various actinide-bearing streams unsuited for evaporation and solidification are treated by a floc precipitation process before discharge. A specific example is at Sellafield (UK) where the solvent wash raffinate, initially a dilute solution of sodium carbonate, hydroxide and nitrate, is neutralised with nitric acid and evaporated to form about 300 litres per day of a solution of nominally 5 M sodium nitrate, according to the THORP flowsheet. The solvent wash raffinate is expected to contain small amounts of actinides (principally about 0.8 g/l of uranium, 8 mg/l of plutonium and 0.3 mg/l of neptunium) that would not warrant recovery. The precipitated sludges are consolidated with cement for eventual deep burial.

2.3.3.7 Discarded solvent

The diluted tributylphosphate (TBP) solvent universally used in industrial nuclear fuel reprocessing plants, although chosen for its chemical and radiolytic stability among other properties, is slowly degraded by radiolysis and hydrolysis. Besides the resultant acid phosphates that are routinely removed by alkaline washes, other deleterious products are formed slowly, both from the TBP and from the organic diluent used. In order to maintain process performance the solvent is renewed by a continuous bleed or by occasional change of inventory. The waste solvent is expected to retain some uranium, plutonium and other actinides. It may be distilled, in which case the actinides would remain in the residue, or be dealt with in some other way (a plant to hydrolyse the waste solvent is being built at Sellafield) to transfer them to an aqueous stream to be treated.

2.3.3.8 Decontamination liquors

Various liquors such as dilute nitric acid, sometimes with added fluoride, or mixtures with organic complexants such as citric acid or ethylenediamine tetraacetic acid (EDTA) are used to remove contaminants from equipment on refurbishment or decommissioning.

2.3.4 Clean-up operations

As ageing fuel recycle facilities and other actinide production and handling facilities are decontaminated and retired from service there will be very large volumes of relatively low radioactivity wastes generated. These will have to be treated and disposed of. The type of treatment required will depend in large measure upon the type of decontamination process used. In many cases it will be desirable to remove the actinides from the large volume of liquid wastes produced. Actinide removal can be greatly simplified if care is taken in the selection of decontamination reagents, and extraneous materials are kept out of the process as much as possible. For example, it would be helpful to avoid the use of actinide complexants unless such complexants were part of a well-thought-out process in which they were useful in a subsequent actinide removal step, or at least did not cause substantial difficulties.

2.3.5 Isotopic source preparation

There are several large-scale isotope production operations that produce actinide wastes. These include, for example, operations to produce ^{238}Pu from ^{237}Np [8,9] for use in isotopic heat sources as well as irradiations in high-flux reactors followed by chemical separations to produce ^{252}Cf for a variety of industrial, medical and research applications [10]. In general, production of these actinides entails fabrication and irradiation of a target in a reactor, producing fission products as well as actinides. The actinide wastes produced are the same as or very similar to those produced in nuclear fuel reprocessing.

2.3.6 Natural and non-nuclear industrial sources

Concern about actinides arising from the nuclear industry needs to be put into perspective. Uranium and thorium minerals are universally distributed as a small fraction of the earth's crust, with substantially higher fractions in ore bodies. Through their daughter elements such as radon, which diffuses from the soil, they are by a wide margin the most important single source of radiation exposure to the general population.

Besides their commercially valuable ores, uranium and thorium also tend to be concentrated in phosphate and rare-earth minerals. Phosphate-containing minerals are mined extensively to produce phosphate compounds for use in industry and as a fertiliser component, and uranium with its daughter elements (notably radium, which is chemically analogous to calcium) occurs in construction materials and fertiliser utilising by-products from its processing. In some circumstances this may add appreciably to the natural radiation dose.

2.4 Orphan fuels

In addition to the large volume of irradiated fuel from power reactors, there is a substantial amount of miscellaneous irradiated fuels which may be characterised as waste. These fuels pose a substantial waste management problem that is probably most acute in the US but is by no means limited to that country. The major nuclear powers, i.e. the US, France, UK and Russia as well as Canada and other European countries, Japan, Republic of Korea, Taiwan ROC and China all have some fuel of this nature. Much of it arose from the early days in the nuclear era when a wide range of experimental and materials testing reactors were being developed, although the bulk of the miscellaneous fuel in the US is irradiated but un-reprocessed US DOE fuel from the plutonium production programme at Hanford.

2.4.1 US DOE fuels

A very wide variety of fuel forms and compositions clad in a large number of different types of fuel claddings are represented by the fuels stored at many of the US DOE sites. Altogether the total mass of US DOE fuel is about 2 675 tonnes of initial (before irradiation) heavy metal (MTIHM). These fuels must be dealt with eventually. The present situation is that they are being stored at sites like Hanford, Savannah River, Idaho Falls and Oak Ridge pending decisions for their final disposal. In some cases, for example the metallic uranium fuel from the “N” reactor at Hanford, the fuel must be repackaged and stored in a new facility to ensure its safe storage until further action is taken. The approximately 2 137 tonnes of “N” reactor fuel comprises nearly 80% of US DOE’s spent fuel. An idea of the amounts and types of all the DOE fuels stored at the US DOE sites may be obtained from any of a number of reports [11,12]. The range of characteristics of the US DOE spent nuclear fuel is shown in Table 2.7.

Table 2.7 US DOE spent fuel characteristics

Characteristic	Attribute
Cladding	Stainless steel, zirconium, aluminium, graphite, no cladding
Fuel “meat” (fissile material within the cladding)	Pure metal, alloy, oxide, hydride, carbide
Enrichment	Depleted to highly enriched uranium
Burn-up	None to highly burned-up
Hazards, by chemical type	Metallic hydrides, metallic carbides, reactive metals, reactive materials, EPA “listed” materials
Size	0.5 to 10 inches diam., 12 to 176 inches long

Section 3

BASIC CHEMICAL DATA

A source of reliable, pertinent basic chemical data is essential to the development of processes that meet the requirements of effectiveness, efficiency, economy and energy conservation. Without an understanding of the underlying chemistry, improvements of existing separation processes and trouble shooting of processes under development is often extremely difficult and costly. Choppin presented a discussion of the solution chemistry of the actinides that addresses oxidation states, co-ordination number, hydration and hydrolysis, complexation, and kinetics [13].

A great deal of actinide separation chemistry is described in the literature, especially as it relates to what is basically thermodynamic information. This includes complexation with both organic and inorganic ligands, equilibria with organic and inorganic ion exchangers, liquid-liquid extraction in aqueous and non-aqueous media, and separations based on electrochemical potentials.

There is a dearth of kinetic information, especially about the rate of attainment of equilibrium among valence states and of extracted species between phases, particularly between liquid phases, and of association and dissociation of actinides with complexing species. There is a limited but rapidly increasing amount of information related to the effects of configuration and configurational modifications of actinide-containing species on separations. This is clearly an important area of research because stereochemical effects are very important in designing ligands for actinide separations.

Finally, there is relatively little information on the separation of actinides using high force fields. The fields that might be employed include for example electrical, magnetic and centrifugal. The work that has been done suggests that separations based on high force fields and field gradients have potential applications in managing actinide-containing wastes.

The purpose of this section is to present a summary of existing actinide chemistry information relating to separations, and to point out gaps and needs for new data. The section is not intended to be an exhaustive compilation of actinide chemistry. Such an undertaking is well beyond the scope of the current report, and has been [14-25], and continues to be [26,27], addressed by other groups.

The basic chemical data required for actinide separation vary between two extremes. For separation of very small amounts of actinides either from a matrix or solution (e.g. a waste in the environment), it is necessary to have a predictive understanding of the system. The amounts of material may be at a sufficiently low concentration so as to make speciation studies difficult, if not impossible. Separation will depend on being able to extrapolate behaviour of an actinide element from markedly different conditions under which it can be more readily studied.

Conversely, macro-separation of actinides is often done in solutions containing high concentrations of dissolved salts, frequently in the presence of an organic phase, in high radiation fields. In such systems fundamental chemical thermodynamic data can only serve as a guideline.

Kinetic measurements done under conditions to elucidate a mechanism may prove useful. However, in the end, measurements relevant to the specific system are required. These need to be in sufficient detail to encompass those chemical conditions that might result from off-normal operation. The more basic thermodynamic and kinetic results will set constraints on what needs to be examined, and will be useful in establishing trends. However, numerical prediction will not be feasible without at least limited experimental work for solutions similar to those used in the process. The establishment of a “base case” is essential prior to the application of the results from more fundamental studies.

3.1 Actinide chemical thermodynamics

Thermodynamic equilibrium information underlies virtually all actinide separations of practical value and importance. For the most part the equilibria involve either those between valence states of a given actinide or those among actinide elements between two phases, whether liquid-liquid, liquid-solid, solid-gas or liquid-gas. In most instances the equilibria are reached rapidly enough relative to the separation process employed that it may be assumed that equilibrium has been attained. However, this is not always the case, and care must be taken to ensure that equilibrium has in fact been reached.

3.1.1 Solutions

The relative stabilities of the valence states for the different elements and the size and charge density of the primary aqueous species in the different oxidation states is important in actinide separations involving aqueous solutions.

3.1.1.1 Ionic radii

Ionic radii in conjunction with ionic charge determine charge density of ions. Charge density plays an important role in determining bond strengths, and particularly in determining complexation behaviour. This is important when elements with similar chemistries are to be separated. At least two reliable sets of ionic radii for An(III,IV) in solids have been published. Shannon’s set [28] is based on values determined from the crystal structures of oxides and trifluorides and is the most frequently used. Another set [29] is based on the structure of the trichlorides. Although the numerical values in the two sets differ, the relative values are similar, showing a gradual (but not smooth) decrease with increasing atomic number. As discussed by Ahrland *et al.* [30], the concept of ionic radius for aqueous species is not very clear, and is especially ill-defined for ions of the type $\text{AnO}_2^+(\text{aq})$ (An = Np, Pu, Am). For the aqueous dioxo-cations the most useful distance is probably some “distance of closest approach” for ligands in the plane of the central metal atom. Some of these have been estimated by Ahrland *et al.* [30], but variations in the hydrolysis and complexation behaviour of protactinium, uranium, neptunium and plutonium indicate that differences in charge distribution may also be important.

3.1.1.2 Oxidation states

Most solution separation methods are based on the differences in the oxidation and reduction behaviour of actinide ions in acidic aqueous media [25]. Thorium exists almost exclusively in the IV oxidation state. Protoactinium is known to exist in both the IV and V oxidation states, but in the

absence of strong complexants (F^- or SO_4^{2-}) forms highly insoluble hydrolysis products even in strongly acidic solutions. Uranium(VI) can be reduced to U(IV), but U(V) is not stable in relation to disproportionation. The main oxidation state for neptunium in aqueous solution is Np(V), although oxidation to Np(VI) and reduction to Np(IV) are quite easy. Np(III) and Np(VII) can be prepared in acidic and basic solutions respectively, but only under special circumstances. Plutonium can readily occur in the III, IV, V and VI oxidation states (sometimes all co-existing in equilibrium in substantial quantities in the same solution). The oxidation state present in a plutonium solution can be affected by radiolysis and the average final oxidation state of the plutonium depends not only on the ionic medium of the solution, but also on the isotopic composition of the plutonium when it is present above tracer levels. Plutonium(VII) may also be formed by strong oxidants in very basic solutions. The oxidation state of trivalent is more important with americium (although Am(IV), Am(V) and Am(VI) can also be formed) and curium solution chemistry is almost exclusively the chemistry of Cm(III). Berkelium occurs in solution as Bk(III) and Bk(IV), californium as Cf(II), Cf(III) and Cf(IV) and einsteinium as Es(III).

Although the differences in the more common oxidation states of uranium, neptunium, plutonium and americium have often been exploited to carry out separations, there is probably scope for developing methods based on the other attainable oxidation states. Development of procedures using strong “holding” oxidising or reducing agents may be feasible. In such cases the redox stability of the solvent may be important. For example, U(III) is thermodynamically unstable in aqueous solutions, and reacts with water to produce hydrogen and U(IV), but may exist as a metastable species for long periods of time if catalysing substances are not present.

Redox potentials of sufficiently high accuracy are indispensable for the evaluation and prediction of the redox behaviours of ions from the viewpoints of both equilibrium and kinetics. Standard potentials of actinide ions in aqueous media determined thermodynamically have been summarised and recommended in the literature [31-33]. However, fairly large discrepancies exist among literature values of the standard potentials, especially for actinide elements other than uranium and plutonium. Even for the data on uranium, discrepancies of more than 0.2 V are still observed. Moreover, the potentials for neptunium and plutonium in basic solutions and for transuranium (TRU) elements are often expressed by values of one significant figure. Even the chemical forms of neptunium and plutonium of different oxidation states have not been fully defined. This is especially so because the elements undergo redox reaction with various components of the system they are in.

One of the main sources of the discrepancies in the literature values is the poor definition of the assumptions on which the calculations are based. For example, the standard potentials for some actinide ions are calculated, not determined directly from experiments (i.e. from the thermodynamic data obtained by calorimetry, emf measurements, etc.) on the assumption that the entropies of trivalent actinide ions are similar to those observed for the Ln(III) ions. The redox potentials determined experimentally by various electrochemical methods and critically evaluated are needed.

Redox potentials reported in the literature for the reversible redox couples, e.g. M(VI)/M(V) and M(IV)/M(III) (where M represents U, Np, Pu) are in fairly good agreement with each other. Those for the irreversible processes, e.g. M(V)/M(IV), show large discrepancies. Such irreversible redox reactions are hard to investigate by ordinary voltammetric or polarographic methods. Hence, special methods must be developed for studies of irreversible electrode reactions.

3.1.1.3 Hydrolysis and complexation

Hydrolysis occurs readily with the actinide elements in their tetravalent and hexavalent states, while trivalent and pentavalent undergo hydrolysis for near neutral (trivalent) or basic (pentavalent) pHs. This attribute contributes to colloid formation and to precipitation of the actinides unless pH is controlled to maintain adequate acidity to prevent them. It may also be used to advantage in separations, although separations based on hydrolytic behaviour are generally not selective. Complexation in many forms finds very broad application in separations of virtually all the actinides.

3.1.1.3.1 Hydrolysis and complex formation with simple inorganic ligands

Compared to the data available for complexation of transition metal ions, relatively good data exist for complexation of actinides ions with simple inorganic ligands. This is particularly the case for complex formation in relatively dilute acidic solutions. As discussed by Ahrlund [25], the actinides generally form stronger complexes with hard ligands (-O-bond) rather than soft ligands (-N-bond or -S-bond). The strength of the complexes depends markedly on the nature of the simplest actinide aqueous ion for each oxidation state, the order being:



Also, in general, the complexes increase in stability with decreasing radius of the aqueous metal ion (although anomalous results have been reported for neptunium relative to uranium and plutonium).

The summary tables from the review by Fuger *et al.* [22] contain no “recommended values” for (a) hydrolysis constants for any of the actinides except uranium; (b) formation constants of carbonate complexes of plutonium in any oxidation state or of Np(IV) or Np(VI); (c) formation constants of phosphato complexes relevant to near neutral solutions for many actinide/phosphate systems; (d) formation constants of arsenato complexes. Of course values of the equilibrium constants for many other complexation and hydrolysis reactions of actinide ions have been reported. Many of these values are unreliable or have not been confirmed. Thus, in many cases, the lack of a recommended value is a reflection of the experimental difficulties in carrying out accurate or appropriate measurements, rather than the paucity of studies or absence of a value in the literature [34]. This is particularly true of hydrolysis studies. The actinide carbonate complexes have more recently been reviewed by Clark *et al.* [35]. The authors conclude that consistent quantitative data are available for An(V) complexation, but indicate that there are still questions as to the complexation constants for An(VI) complexes (except for uranium). The review also suggests that more studies of the complicated aqueous chemistry of An(IV) in carbonate media are required.

Considerable work related to hydrolysis has appeared since 1989 (the latest date for references cited by Fuger *et al.* [22]), most particularly the studies of Pu(VI) by Pashaladis *et al.* [36,37], the Pu(V) hydrolysis and carbonate complexation study by Bennett *et al.* [38] and the UO₂ solubility study of Rai *et al.* [39]. Neck *et al.* [40] remeasured the solubility of hydrated NpO₂OH(s) in basic solution in an attempt to resolve uncertainties in the hydrolysis constant. However, two recent attempts to determine the enthalpy of formation of the hydroxide [41,42] are not in good agreement. Grenthe and Lagerman [43] have reported a study of hydrolysis of U(VI) in sulphate media, and their analysis includes a discussion of the possible formation of mixed hydroxy-sulphate complexes. Sandino and Bruno [44] have reported on a study of complexation of U(VI) with phosphate in near neutral solutions, a study that also yielded a value for the formation constant of UO₂(OH)₂(aq).

The actinides form many polymeric hydrolysis species and aggregates that may interfere with separation processes. These are discussed further in Section 3.1.1.4.

Actinide separations must often be carried out under process conditions or from waste streams differing greatly from the conditions and compositions of the solutions used for more fundamental studies. Therefore, even though there is an ongoing need for more basic work to elucidate the simple hydrolysis products and simple inorganic complexes of the actinide aqueous ions, there also is a need to extend this work to more complicated solutions. Such work not only involves determining the formation constants for higher order complexes, but also might include (a) complexation in solutions having very high salt concentrations for which standard interaction theories either do not apply (e.g. the SIT) or require much additional data (e.g. Pitzer equation); (b) more studies of formation of mixed complexes, especially hydrolytic mixed complexes; (c) complexation at temperatures far from the ubiquitous 25°C; and (d) studies of actinide complexation in solutions saturated with organic solvents.

3.1.1.3.2 Complexes with simple organic ligands

Actinide complexation with simple organic ligands can be used to represent decomposition products of organic compounds that have contacted actinide-bearing media (e.g. soils). Simple carboxylic acids form weak actinide complexes [45]. For neutral and basic solutions, hydrolysis tends to predominate, and complexation with carbonate and phosphate may also be important.

Other simple organic ligands result from the degradation of extractants and solvents used in large-scale actinide separations. Among these are the relatively well studied mono and dialkyl phosphates. The most important of these from an actinide separations point of view are mono and dibutyl phosphate, the hydrolysis products of tributylphosphate.

TBP, which is an ester of phosphoric acid, has been discussed by Schulz and Navratil [46]. TBP is susceptible to hydrolysis reactions that produce, successively, butyl alcohol plus dibutyl phosphoric acid (HDBP), butyl alcohol plus monobutyl phosphoric acid (H₂MBP), and finally, butyl alcohol and phosphoric acid. Any or all of these hydrolysis products can be present. The presence of various chemical species in the water may increase or decrease the rate of hydrolysis. Species studied include nitric acid and a variety of metal ions. Metal ion valence state influences its effect. TBP hydrolysis products may be removed from TBP or solutions of TBP in organic diluents. Removal methods include washing with basic solutions [47], sorption of degradation products on solid sorbents [48] and distillation [49].

Some multidentate ligands, often used in the nuclear industry as chelating agents in the cleaning of corrosion products from reactor systems, have relatively strong affinities for actinide ions in aqueous solutions. Thus, for example, low concentrations of EDTA can enhance the solubilities of actinides in neutral and weakly acidic solutions. There is a need to remove such materials from wastes and waste streams. For example, a summary of the relatively sparse data available for EDTA complexes based on the critical assessment of Anderegg [50] is presented in Table 3.1. Ahrland [25] noted that for the dioxo-actinide ions, the probability is high that polymeric species are formed. (This statement must be qualified, because polymers do not form at tracer levels.) For the less common chelating agents, the values are even less well known, and further work, particularly involving studies using competitive complexants in neutral and basic solutions, is required.

Table 3.1. EDTA complexation constants with aqueous actinide ions

M^{n+}	T/°C	Ionic strength	$\log_{10}K_{ML}$	$\log_{10}K_{M(HL)}$	pK of ML
Th ⁴⁺	20	0.1	23.25±0.11*		1.98
U ⁴⁺	25	0.1	25.8±0.2		4.72
UO ₂ ²⁺	25	0.1		7.36±0.05	
Np ⁴⁺	(25±2)	1	24.55		
NpO ₂ ²⁺	24	0.1	7.33±0.06*	5.30±0.08*	11.51±0.08
NpO ₂ ²⁺	25	0.1		7.36±0.05	
Pu ³⁺	20	0.1 (KCl)	18.12		
Pu ^{IV} (OH) _x	20	0.1 (KCl)	17.66		
PuO ₂ ²⁺	25	0.1		4.80±0.08*	
PuO ₂ ²⁺	No usable value				
Am ³⁺	20	0.1	16.91±0.09		
	25	0.1	17.00(?)±0.04		
Cm ³⁺	20	0.1	17.10(?)±0.04		
	25	0.1	17.10±0.05		
Cf ³⁺	20	0.1	17.9		

* Tentative value

3.1.1.3.3 Complexes with polyorganic acids

Complexes with naturally occurring polyorganic acids can persist to quite high pH values. Because of the nature of humic and fulvic acid materials, it is not possible to define a unique set of thermodynamic parameters for their interaction with metal ions in solution. Material from different sources may behave differently. The apparent protonation constants of the large molecular weight polyelectrolytes which are referred to as humic acid vary with pH, as do the binding constants of the humates with a particular cation, the number of acid groups per gram of sample and the pH value at which the degree of ionisation equals 0.5. Data for fulvic acids are not as extensive, but the complexation behaviour of humates and fulvates is similar. Studies have been carried out with various actinides in all of the common oxidation states. The carboxylic acid groups are probably the primary binding sites. Because of increasing hydrolysis at higher pH, the humate and fulvate complexes are not important for An(IV), but complexation with An(III) may be strong as competitive hydrolysis is less than for An(IV). Further studies using organic materials from different sources would be useful [51].

3.1.1.4 Hydrolytic polymers, solubility and colloid formation

Many highly charged aqueous cations in sufficiently high concentration in acidic solutions hydrolyse to form polymeric species when the pH increased. In some cases, if the metal ion concentrations and the rate of polymer formation are sufficiently high, the aggregates may become large enough to be considered colloids.

The lower size limit for colloids (as opposed to polymeric solution species) is arbitrary, and is often based on the nominal size limit of the ultrafilter membranes used in colloid studies. A lower limit of 1 nm is often used [52]; this corresponds to a "nominal molecular weight limit" (NMWL) of 10 000 based on a calibration with organic macromolecules.

In water that is not flowing, the maximum size of a particle for which Brownian motion cannot overcome sedimentation due to gravitational forces is a function of the particle size and density. Vilks calculated that for particles with a density from 1.1 to 2.0 g/cm³ the sedimentation limit varies from 600 to 250 nm. An arbitrary size of 450 nm is often used in the geochemical literature [52] as the boundary value between large colloids and small particles.

The most frequently and intensively studied actinide colloid has probably been the Pu(IV) hydroxide polymer. This species can be a problem in separations, as it forms easily at low pH and, as often is the case with such species, is very slow to depolymerise if a solution is acidified. This is especially true for aged polymer. The stability of the polymer and the tendency toward aggregation of primary particles is dependent on the nature of the anions in the solution and the anion-to-plutonium ratio [50]. The crystallinity of the primary particles may change with time, and may depend on the isotopic composition of the plutonium [53]. More data as functions of ionic strength, specific anion concentrations and temperature are required. Kim [54] notes that hydrolytic colloids of actinides (americium in particular) can form even in solutions that are very dilute in the actinide element. Similar considerations apply to the behaviour of smaller hydrolytic polymers.

In considering waste stream treatment it should be recognised that the sorption of actinide species onto natural colloids and onto colloids resulting from etching of waste forms or corrosion of containers constitutes a possible mode of actinide transport. Natural colloids can include residual inorganic materials from the weathering of minerals (e.g. silica or alumina), hydrolysed precipitates of heavy metal ions and organic macromolecules [55]. For the most part, the sorption onto organic colloids can be considered equivalent to complexation with humates and fulvates (discussed above). Vilks [52] indicates the need for further work in characterising natural colloids and the development of a model for colloid transfer in fractured rock. In particular, the reversibility of sorption of actinides onto natural colloids requires further investigation. Lieser and Hill [56] compare the hydrolysis and colloid formation of thorium and uranium and conclude that in groundwater the colloid fraction of thorium consists mainly of carrier colloids.

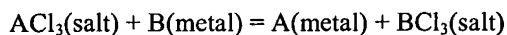
3.1.1.5 Sorption/desorption

When actinides in solution are handled at extremely low concentrations the question arises as to the degree of their sorption on surfaces of their container or on other extended surfaces in contact with the solution, particularly at pH values where hydrolysis can occur. At very low concentrations sorption may account for a significant fraction of the actinide present. The importance of this phenomenon is twofold. First, the results of experimental studies may be vitiated by inadvertent and unknown loss of the actinides to the surfaces. Second, the surfaces may become contaminated by α -emitting nuclides. On the other hand, the phenomenon may be used to advantage to deliberately remove low concentrations of actinides from solutions.

Ichikawa [57] reports on the adsorption and desorption of ²³⁸Pu(IV) from extremely dilute solutions (10⁻¹¹ M) onto glass and polyethylene and found two different types of adsorption. One occurs at pH values below 6, with a maximum adsorption at pH 3 to 4. It is distributed homogeneously and decreases with increasing salt concentration. It appears to be due to ionic plutonium. The other occurs at pH values between 6.5 and 10, and it appears to be due to colloidal plutonium. Caceci and Choppin [58] report on ways to reduce the loss from neutral solutions of Am(III) and uranyl ion to acceptable levels for experimental purposes.

3.1.1.6 Non-aqueous media

An important non-aqueous separation processes is electrochemical refining. In general, electrochemical cells consisting of fused salt electrolytes (mostly eutectic mixtures of the fluorides or chlorides of the alkali metals) and fused metal electrodes are used. In simplified form, the equilibrium distribution of two actinide elements between the metal and the salt is determined by the reaction:



The equilibrium constant K for the above reaction is:

$$K = \frac{[a_A][a_{BCl_3}]}{[a_{ACl_3}][a_B]} = \exp(-\Delta G^0 / RT)$$

where a is the activity of a compound in the fused salt or fused metal, ΔG^0 is the Gibbs energy of reaction, R is the gas constant and T is the absolute temperature. Thus, for the understanding and modelling of this process knowledge of the following data are essential:

- i. Gibbs energies of formation of the actinide halides (III and IV oxidation state);
- ii. activities (or activity coefficients) of actinide (III,IV) halides in fused salts (chlorides and fluorides);
- iii. activities (or activity coefficients) of the actinide metals in fused metals (e.g. cadmium, bismuth, zinc).

3.1.1.6.1 Gibbs energies of formation of halides

The Gibbs energies of formation of the tri- and tetrafluorides of thorium (ThF_4), uranium (UF_3 , UF_4) and plutonium (PuF_3 , PuF_4) are fairly well established, though there is still some dispute about the enthalpy of formation of uranium tri- and tetrafluoride [20]. This is related to a systematic but unexplained difference in the results from solution calorimetric [59] and fluorine-combustion calorimetric techniques [60], but in view of the accuracy of the data for the fluorides of the other actinide elements, the uncertainties for UF_3 and UF_4 are acceptable. The available data for Gibbs energies of formation of the tri- and tetrafluorides of protactinium, neptunium, americium and curium are solely based on estimates [20], relying on the data for the fluorides of thorium, uranium and plutonium and of the lanthanide elements. For the enthalpies of formation, this leads to reliable results, but the data for the entropies and heat capacities are subject to considerable uncertainties as the theoretical basis and the experimental support for such (empirical) estimation methods is still poor.

Also for the tri- and tetrachlorides, the Gibbs energies of formation for the compounds of thorium ($ThCl_4$), uranium (UCl_4 , UCl_3) and plutonium ($PuCl_3$) are well established [20]. The Gibbs energies of formation of the tri- and tetrachlorides of protactinium, neptunium, americium and curium are subject to considerably larger uncertainties.

The enthalpies of formation of some of these compounds ($PaCl_4$, $AmCl_3$, $NpCl_4$) have been measured using microcalorimetric techniques [61-63], for the other compounds estimates are available [20]. The entropies and heat capacities of these compounds have not been measured and only estimates are available [20].

3.1.2 Solids

3.1.2.1 Gibbs energies of formation

The actinide halides and oxides are an important class of compounds in non-aqueous actinide separation processes. A large number of references exist for these compounds [64-66]. There are separation processes based on selective formation and volatility of these compounds, and on their behaviour in systems of specific process importance, such as molten salts.

3.1.2.2 Solid waste phases

The solid phases present in actinide oxide and halide wastes may be extraordinarily complex. The complexity reflects both the inherent complexity of the 5f electron elements and the nature of the processes that produced the wastes containing the elements. In some processes, for example those used to produce and to recycle weapons plutonium, metallic plutonium may be present with fluorides, or mixtures of alkali metal and plutonium chlorides.

In processes like that being demonstrated for the reprocessing of metallic U/Zr fuel and metallic uranium blanket [67], wastes may be produced that contain metallic phases such as cadmium, zinc, magnesium or copper in addition to small fractions of plutonium either as metal or chloride.

Actinides are often found in refractory wastes such as crucibles used for the preparations of metals and in ashes from incineration of wastes such as organic ion exchangers. Such wastes are not well characterised and have seldom been subjected to complete analysis of all the phases present. They are often quite chemically complex. Nonetheless, knowledge of the chemical phases present can be useful when considering methods for removing the actinides from the refractory matrices. This problem is discussed further in Section 4.1.5.2.

3.1.2.3 Actinides in refractory matrices

Actinides are often contained in refractory matrices formed during the foundry casting of actinide metals and the incineration of actinide bearing wastes. Graphite is the major constituent of certain foundry residues, and silica and alumina are the major constituents of incineration residues. From the point of view of actinide-containing waste stream treatment, the most important actinide-containing refractory residues are those containing PuO_2 . Therefore the separation of residual plutonium from PuO_2 /graphite and PuO_2 /silica or PuO_2 /alumina mixtures to reduce the volume of actinide wastes are of interest. Aqueous biphasic extraction offers the potential for yielding very high separation factors among metal oxides, silicates and aluminosilicates [68]. Any one of a large number of extractants may be useful for the extraction of plutonium from the insoluble matrices after the plutonium has been solubilised. Grinding to an average size of about one micron is probably necessary to release PuO_2 particulates from the refractory matrices.

3.1.3 Volatile compounds

Not many pure actinide metals or actinides in alloys or in mixtures with other metals are volatile enough to provide a basis for their separation. Americium is an exception. On the other hand, the halides of several of the actinides, especially the fluorides, are quite volatile, and provide a basis for

the selective separation of those actinides from a wide variety of other elements. The chlorides are also volatile, but because many other metals form highly volatile chlorides the chlorides are not as widely used as the fluorides for separations.

3.1.3.1 Volatility of metals

The volatility of actinide metals and their alloys or mixtures has not been much used in relatively large-scale processing to achieve their separation from one another or from other metals or compounds. Separations on a small scale for analytical purposes and for research have, however, been carried out.

3.1.3.1.1 Pure metals

Reliable data for the volatility of most actinide metals are available for the pure metals of the series actinium (Ac) to einsteinium (Es) [69]. The vapour pressures differ by several orders of magnitude in this range. In general, the heavier actinides are considerably more volatile than the lighter ones. The volatility of americium is especially high (see Section 4.2.4.2).

3.1.3.1.2 Solutions of metals

For (possible) separation techniques the vapour pressure above actinide mixtures is much more important than that of the pure compounds. Quantitative experimental results for mixtures are limited to the study by Erway and Simpson [70] who measured the vapour pressure of americium above a dilute solution ($x_{Am} = 10^{-5}$) in plutonium. Moreover, little is known about the solution behaviour of actinide mixtures.

3.1.3.2 Volatility of fluorides

The hexafluorides of the uranium, neptunium and plutonium are highly volatile, as has been reported in several concordant studies. The vapour pressures and the boiling or sublimation points of these compounds are close (see Table 3.2) and, hence, mutual separation on the basis of volatility is difficult but separation from other elements which do not form volatile (hexa)fluorides, is not. Some degree of separation can possibly be achieved by the selection of fluorination conditions: UF_6 is easier to form and more stable than PuF_6 so oxidation of MOX fuel followed by preferential fluorination of uranium to the hexafluoride can be used to selectively form $UF_6(g)$ while leaving plutonium as the much less volatile $PuF_4(s)$.

Table 3.2 The boiling or sublimation points of some AnF_6 compounds [71]
(1 atm=101.325 kPa)

Compound	Boiling/sublimation point, K
UF_6	329.69
NpF_6	328.33
PuF_6	335.31

The volatility of the lower fluorides is considerably less, but systematic studies of the stabilities of gaseous AnF_n ($n < 6$) compounds have only been made for the Th-F and U-F systems. From the point of view of actinide separation, these compounds are not very useful. A discussion of the practical application of the volatility of actinide fluorides is presented in Section 4.2.4.1.

3.1.3.3 Volatility of chlorides

Only uranium is known to form a hexachloride compound which is volatile at relatively low temperatures. However, UCl_6 is rather unstable and dissociates to lower uranium chlorides and chlorine gas at temperatures above 120°C . This effect is most likely the origin of the discrepancy between the two vapour pressure studies that have been made for this compound [72,73].

Volatile AnCl_5 compounds have been reported for uranium and protactinium and also the lower chlorides of uranium (UCl_4 , UCl_3) and plutonium (PuCl_4 , PuCl_3) are known. As is the case for the lower valent actinide fluorides, these compounds are not very useful in separations. For a discussion of the use of volatile chlorides in separation, see Section 4.2.4.3.

3.2 Radiolysis

The exceptional chemical complexity of the actinides is still further complicated by their radioactivity. Radiation effects are manifested primarily in solutions of the actinides, although in the case of short-lived, energetic α -emitters such as ^{242}Cm and ^{238}Pu there can be radiation effects in the solid phase and the gas phase (e.g. the radiation-induced decomposition of PuF_6). In general, α -emitting actinide isotopes produce more effects of radiation per decay than do the β - γ emitting isotopes because an α -emitting isotope deposits a larger fraction of its decay energy in the medium containing the isotope than a β - γ emitter does, and the α decay energy is usually several times larger. In fuel reprocessing wastes that contain fission products in addition to actinides, the source of radiation is mostly the fission products. However, the chemical effects are essentially the same as for the actinides alone.

The rates of reaction of radiolysis products with actinide ions has been the subject of less study than might be expected. Vladimirova summarises the behaviour of neptunium species in nitric acid solutions [74] and Pikaev *et al.* [75] discuss the results of pulse radiolysis studies for actinide ions. Most of the results existant are for acidic solutions, with a few experiments having been done for neutral or basic solutions [76]. However, see Pikaev *et al.* [77], in which it was found that the addition of EDTA, formate ion and alcohols considerably increased radiation-induced reduction yields.

In aqueous solution it is usually the formation of short-lived hydrated electrons, hydrogen atoms, hydroxyl radicals and hydroperoxide radicals that lead to chemical reactions. Hydrogen peroxide, a long-lived radiolysis product, is also formed and can have important chemical effects [78]. The hydrated electron is a strong reducing agent. The hydrogen atom is a somewhat weaker and slower reducing agent than the hydrated electron, but is important in acidic media. The hydroxyl radical is a strong oxidising agent; hydrogen peroxide may be either an oxidising or reducing agent depending on the actinide ion and the solution pH. The effect of these radiolytic moieties on actinides is a strong function of pH, solution composition, and the redox potentials of the specific actinide.

Yields of primary products of water radiolysis presented as G-values are given in Table 3.3 for γ -rays (^{60}Co) and high-energy electrons, and in Table 3.4 for α particles.

Table 3.3 G-values* for primary radiolysis products in bulk solution for ^{60}Co γ rays and electrons with energies above 1 MeV [79]

pH	e_{aq}^-	H^\bullet	OH^\bullet	O^\bullet	H_2	H_2O_2	$\text{H}^\bullet_{\text{aq}}$	OH^-_{aq}
0-2	3.05	0.6	2.95	0.0067	0.45	0.8	-	-
4-9	2.8-2.9	0.6	2.8-2.9	0.0067	0.45	0.75	3.3-3.4	0.5-0.6
12-13	2.8-2.9	0.55	2.9	0.012	0.4	0.75	-	-

* The term "G-value" used here is the number of atoms, molecules, radicals or other identified species produced per 100 eV of energy sorbed in the medium irradiated. The modern G-value is defined as moles/joule in the SI-system, conversion factor 1 mole/joule = 9.65×10^6 molecules per 100 eV.

Table 3.4 G-values for primary radiolysis products in bulk solution for α particles with energies of 5 to 6 MeV or from ^{210}Po

Energy MeV	Aqueous medium	$e_{\text{aq}}^- + \text{H}^\bullet$	OH^\bullet	H_2	H_2O_2	HO^\bullet_2	Refs.
5.3	0.4 M H_2SO_4	0.55	0.35	1.4	1.3	0.2	[80]
6.4	pH 7	-	0.4	-	0.95	0.085	[81]

Radiolysis is especially important in the actinides separation processes based on solvent extraction and ion exchange. In these instances the solvent or ion exchanger is usually organic. The effects of radiation on ion exchangers is discussed in Section 4.1.3.1.2. The effects of radiation on the important solvent TBP were discussed by Davis [82] and more recently by Kuno and Hina [83]. In general, both the extractant and the organic diluent are subject to radiolysis [84], yielding radiolytic products that can interfere with the actinide separation sought. Radiolysis may also affect the oxidation state of elements being extracted, while many of the species in process solutions may act as scavengers for radiolysis products. Normal paraffinic hydrocarbons (NPH) are often used as diluents for TBP. In extractions involving TBP, NPH and nitric acid, γ radiation produces organic degradation products such as alkanes, nitro and nitrite compounds, saturated and unsaturated alcohols, nitro alcohols, nitro alkenes, ketones and carboxylic acids [84]. Degradation rates are observed to increase with increasing nitric acid concentration and increasing temperature. There may be about an order of magnitude increase in degradation rate as the temperature is raised from 25°C to 100-108°C. Sparging to remove nitrogen dioxide substantially reduces radiation damage. Plutonium has been found to be retained in irradiated diluent even in the absence of TBP. Degradation of NPH can also cause serious phase separation problems when degradation products are as low as 10^{-3} M.

Radiolysis has also been observed in the case of inorganic salts [85]. An important instance of an inorganic actinide waste that has undergone substantial radiolysis is found in connection with the Molten Salt Reactor Experiment (MSRE) at Oak Ridge National Laboratory [86]. In this case a molten alkali metal fluoride salt system was the reactor fuel. Upon termination of the reactor experiment the fuel salt became a waste that was permitted to set in solid form for several decades. During that time the decay of the uranium (a mixture of ^{233}U and ^{235}U tetrafluorides) produced UF_6 , lower-valence forms of uranium, and fluorine gas from radiolysis of the UF_4 in the fuel salt.

3.3 Actinide analysis related to separation processes

Advances are continually being made in approaches to methods of analysis for separation processes [87]. Many of these advances are directed at reducing the volume and chemical nature of the wastes produced during the analysis itself [88]. Others are directed toward improved process monitoring; still others are directed toward the analysis of packaged wastes. More advanced techniques such as intense-light-source and photoacoustic methods (PAS) hold considerable promise. PAS is already used routinely in the 10^{-5} to 10^{-9} M concentration range; laser fluorescence excitation can measure curium at 10^{-12} M [89].

3.3.1 Analysis in liquids and solids

Solids are seldom analysed as such for actinides, but are generally dissolved so that standard analysis methods for liquids can be applied. The most important methods are X-ray fluorescence for uranium and radiometry for other actinides, if necessary after chemical separation from interfering species.

3.3.1.1 Packaged (or “workshop”) wastes

The most explored instrumental nuclear and non-nuclear methods for *in situ* analyses of trace impurities in solid consist of γ -spectrometry, mass spectrometry and neutron activation analyses. Measurements *in situ* using portable γ spectrometers have been already routinely performed and the results were compared with those obtained from the analyses carried out in the laboratory [90-95]. For the latter two methods mentioned, portable instruments are still under investigation and only prototypes exist.

It has been demonstrated that a portable γ -ray spectrometer must be used with caution when uranium concentrations in soils are needed [91]. Subterranean *in situ* measurements of the following actinides isotopes, ^{235}U , ^{238}U , ^{237}Np , ^{239}Pu , ^{241}Pu and ^{241}Am have been simultaneously performed at 10 nCi/g (370 Bq/g) level in less than seven minutes utilising high-resolution germanium diode γ -ray spectroscopy. Measurements of plutonium and americium have been performed using a planar germanium detector in contaminated laboratories and buildings. It has been found that the detection limits depend on local background activity.

3.3.1.2 At the laboratory

Laser resonance ionisation mass spectrometry has been investigated as a detection method for trace amounts of actinides [96-99]. Using this process high sensitivity and selectivity can be achieved.

Resonance ionisation mass spectrometry (RIMS) has been applied for elemental and isotopic composition [100-104] of uranium and plutonium. RIMS technique offers the advantage of high elemental selectivity compared to the conventional thermal ionisation mass spectrometry.

Traces of uranium and thorium have been determined in aluminium with flow injection (FI) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [105]. Limits of detection (LOD) of 0.2 ng/g have been obtained.

LA-ICP-MS has been used to perform semi-quantitative determination of impurities in uranium oxide certified reference materials (CRM) [106]. LODs for low m/z (atomic mass/atomic number) elements were found to be about 1 fg/g; high m/z elements had LODs approximately 100 times lower. LA-ICP-MS operated in a mobile laboratory has been described by some authors [107,108] to rapidly detect ^{230}Th activity levels in soil samples.

Neutron activation analysis has been extensively employed for the determination of trace amounts of uranium and thorium in different types of samples as well as for trace impurities in uranium oxides [109-130]. Delayed neutron activation analysis (DNAA) has been used to determine uranium concentrations in human tissues. The method gives results that are rapid, sensitive and highly selective.

A method has been developed for the determination of ng/g levels of uranium in reactor materials by neutron activation analysis and the procedure has been applied to the determination of uranium in various materials used in the Japan Materials Testing Reactor (JMTR). Uranium concentration was of the order of ng/g in each type of sample tested. Agreement was satisfactory between the results and the certified values for reference materials tested.

Neutron activation analysis using epithermal neutrons has been employed for the determination of trace amounts of uranium in coal and petroleum. The content of uranium in oils was found to be 32~108 ng/g, whereas the content of uranium in coals was in the range from 0.6 to 3.2 fg/g [128]. There appears to be an inverse correlation between coal content and uranium content. The variation of uranium content among these materials was explained in terms of the chemical properties of uranium in relation to organic ligands.

3.3.1.3 Other

There are several methods for analysing actinides, most of which capitalise on the fact that many actinides emit energetic α particles which can be discriminated easily from β - and γ -rays by the use of conventional detectors and associated electronic equipment. A method that has become a standard procedure because of its accuracy and sensitivity, and because it has applications for actinide analysis in a wide variety of situations (both in process control and in environmental analyses) is liquid scintillation α spectrometry [131]. This method, which goes by the trade name PERALS, employs selective extraction of actinides from aqueous samples into an organic phase containing a compound that scintillates upon interaction with an α particle. The emitted light is detected by a photomultiplier tube and associated electronics that measure the energy and quantity of α emission, thus identifying and quantifying the actinides. The measurement equipment and kits to carry out the sample preparation and solvent extraction are commercially available.

Section 4

STATE OF THE ART IN ACTINIDE SEPARATION CHEMISTRY

There is a vast amount of information on actinide separation chemistry in books, technical journals and reports from laboratories around the world. The reason for this abundance of information resides in the importance of the actinides both for the production of nuclear weapons and for nuclear power production. One of the earliest books in the field is the classic work on radiochemistry by Friedlander and Kennedy [132]. Following the first Geneva Conference [133] Benedict and Pigford [134] summarised a great deal of the separations information presented at the conference. This work was followed shortly afterward by Peterson and Wymer's [135] book on the chemistry of the nuclear fuel cycle. In 1967 an English translation of the 1961 USSR book on complexes of the transuranics by Gel'man *et al.* [136] was published, and in 1981 Wymer and Vondra edited a volume on the light water reactor nuclear fuel cycle [137]. Choppin *et al.* published extensively on actinide separations science [138] and technology [139]. For the most part the separation chemistry reported has been in aqueous solution. However, there are many important exceptions where separations based upon both high temperature, non-aqueous solution chemistry and volatility. Much of this separations work was done in classified weapons production laboratories and so has not been as extensively reported as the more commercially oriented aqueous separation chemistry. A review of both aqueous and pyrochemical reprocessing of actinide fuels has recently been provided by Toth *et al.* [140]. Some of the more important and useful developments in separation chemistry are discussed below.

4.1 Hydrometallurgy

Broadly speaking many of the separation processes used in the nuclear industry may be categorised as hydrometallurgical processes. They involve the use of aqueous reagents to solubilise metals in ores and in various materials to be processed. Often the aqueous process streams are used in conjunction with liquid or solid organic process materials. Early processes for isolating, concentrating and purifying actinides were primarily hydrometallurgical. Today the principal reprocessing method for LWR spent fuel, the PUREX process, is a hydrometallurgical process, as are most of the processes being developed specifically for treatment of actinide wastes.

4.1.1 Liquid-liquid extraction

Although the first large scale process for separating plutonium from irradiated uranium was a precipitation process – the bismuth phosphate process – that process was soon replaced by a solvent extraction process employing a ketone solvent and an aqueous stream of actinides and fission products from irradiated fuel, which was dissolved in nitric acid and salted with aluminium nitrate. Liquid-liquid extraction has the advantages of ease of remote operation, reagent recycle and process control. Madic [141] presents a summary overview of separation of actinides by liquid-liquid extraction.

4.1.1.1 PUREX

The PUREX process is the predominant method for reprocessing commercial reactor fuel throughout the world. Although numerous process improvements have been made over the years since its introduction [142-144], the process is basically the same as it has been for over forty years. It involves contacting a nitric acid solution of dissolved irradiated fuel with an organic solution of TBP in a hydrocarbon such as odourless kerosene or dodecane. Typically the TBP concentration is about 30%, although the concentration may be varied to effect a specific separation. The PUREX process is based on the fact that TBP selectively extracts hexavalent uranium and tetravalent plutonium from moderately concentrated (~ 3 M) nitric acid solutions. Conditions may also be adjusted to extract neptunium. If the TBP solution of extracted actinides is subsequently contacted with dilute (~ 0.1 M) nitric acid the actinides may be easily back-extracted, i.e. "stripped", into the dilute acid. By adjusting the valence of plutonium from tetravalent to trivalent, it may be extracted (partitioned) from the organic solution to the aqueous solution, thus providing an effective means of separating (partitioning) the plutonium from the uranium.

The PUREX process may find application as a preliminary separation step in processing actinide-containing wastes. Although it is probably not efficient enough to reach the very low levels required for removing actinides from wastes to the level necessary to make them "non-TRU" wastes, it could provide a suitably clean feed stream for a subsequent more efficient process [145].

4.1.1.2 IMPUREX

Schmieder and Petrich [146] have described a one-cycle PUREX process which was demonstrated in a small pilot unit. The success of their process was dependent in large part on use of a computer model for solvent extraction to predict what the plutonium concentration profile looked like as a function of operating conditions at various stages of extraction. (Although only a single cycle of solvent extraction is employed, an additional clean-up step employing a continuous crystallisation of the plutonium and uranium extraction products is postulated.) The methodology they employed to devise their predictive computer model may find application in optimisation of extractions related to actinide waste processing.

4.1.1.3 TRUEX

TRUEX [147,148] is a solvent extraction process designed to separate TRU elements from the aqueous nitrate or chloride waste solutions that are typically generated in reprocessing plant or plutonium production and purification operations. The resulting aqueous solutions are intended to be sufficiently separated from TRU elements to be disposed of as non-TRU wastes. The key ingredient in the TRUEX solvent is octyl (phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, more simply called CMPO. This compound is combined with TBP and a diluent to form the extractant. The diluent commonly used is a normal paraffinic hydrocarbon having twelve carbon atoms. CMPO concentrations may be about 0.2 M; TBP may be about 1.0 M. In 3 M nitric acid all the actinides except Np(V) show very large distribution ratios. At nitric acid concentrations down to 0.1 M the distribution ratios decrease by more than an order of magnitude, but remain as large as 10 for plutonium and uranium. Lanthanide elements such as europium (Eu), cerium (Ce) and praseodymium (Pr) behave similarly to the trivalent actinide, Am(III). Other fission products with the exception of zirconium (Zr) show relatively small distribution ratios. Zirconium is extractable, but its extraction may be suppressed by the addition of oxalic acid to complex it. The behaviour of Ru is notoriously unpredictable. Total metal ion concentration in the aqueous feed must be kept to values low enough to

prevent third-phase formation. Because tetra- and hexavalent metals such as plutonium and uranium are very extractable in CMPO solvent, stripping with dilute nitric acid is not feasible, and more aggressive stripping, for example with the powerful diphosphonate actinide extractants (see Section 4.1.1.9.4), is required.

4.1.1.4 DIAMEX

The DIAMEX [149-151] process is a solvent extraction process for TRU elements. Developed in France, it claims the advantage over processes employing phosphorous-based extractants in that the solvent is totally combustible. In this process amides are dissolved in alkanes and used to extract TRU elements from nitric acid solutions. Trivalent lanthanide nitrates are also extracted, and therefore a second extraction step is necessary to accomplish the separation of actinides from lanthanides. Alkylated derivatives of tripyridyltriazine may be used for this step. A typical diamide used is dimethyldibutyltetradecylmalonamide (DMDBTDMA). Advantages claimed are low reagent solubility in nitric acid, extraction with controllable third phase formation, and good radiation and thermal stability. Zirconium(IV) nitrate extracts better than either the lanthanides or actinides, but its extraction may be reduced to acceptable levels by complexing it with oxalic acid or ketomalonic acid. Extraction of molybdenum may be suppressed by complexation with hydrogen peroxide. Iron, which is almost always present from corrosion of process equipment, also has a high affinity for DMDBTDMA, but Fe(III) extracts slowly both into and out of the organic phase, and it may be possible to use this property to separate it from the actinides and lanthanides. Amides with improved properties for the separation of the more difficult actinides such as trivalent americium are being sought in the continued development of this process.

4.1.1.5 TRPO

The extraction of actinides and lanthanides by trialkyl (C_6 - C_8) phosphine oxide (TRPO) has been studied at the Institute of Nuclear Energy and Technology of Tsinghua University and Beijing Institute of Nuclear Engineering in China. It was found [152] that >99% of U(VI), Np(IV), Np(VI), and Pu(VI) in 0.2 to 1 M nitric acid were extracted through one-stage extraction with 30 vol.% TRPO-kerosene. Also, >95% of Pu(III), Am(III) and Ln(III) could be extracted, while a much smaller percentage of fission products such as Sr, Cs and Ru were extracted. The stripping behaviour of actinides loaded in 30 vol.% TRPO-kerosene was studied [153], and Am(III) and the Ln(III) ions were stripped with sodium carbonate. A flowsheet for the removal of actinides from high-level liquid wastes (HLLW) by TRPO extraction was proposed and verified by multi-stage counter-current cascade extraction experiments with synthetic HLLW [154].

TRPO, with its relatively low cost and its high extraction efficiency, is a promising reagent for separation processes. The TRPO-based process, however, has some disadvantages. It works only at a relatively low nitric acid concentration (0.1 to 1 M), and therefore HLLW from reprocessing has to be deacidified before extraction. Moreover, Ln(III) ions cannot be separated from transplutonium elements by the extraction process recommended so far.

4.1.1.6 DIDPA extraction

Studies on the extraction behaviour of actinides and other fission product elements with the novel extractant di-isodecylphosphoric acid (DIDPA) have been carried out by Kubota *et al.* of Japan Atomic Energy Research Institute (JAERI) in order to develop a partitioning procedure of the

elements in HLLW [155,156]. The DIDPA extraction is advantageous for the partitioning of the transuranium group. Am(III) and Cm(III) can be extracted from a solution of low acidity such as 0.5 M nitric acid and both tetra- and hexavalent U, Np, and Pu ions, and even neptunium in pentavalent can be extracted. Trivalent ions can be separated from tetravalent ions by appropriate back-extraction procedures.

The feasibility of the separation process proposed was demonstrated with a mixer-settler of seven stages using an actual HLLW. It was confirmed that more than 98% of plutonium was extracted with 30% TBP and more than 99.99% of americium and curium with 0.5 M DIDPA + 0.1 M TBP. It was noteworthy that even Np(V) is extracted by DIDPA. The oxidation state of neptunium extracted with DIDPA from 0.5 M nitric acid solution with hydrogen peroxide was tetravalent in the organic phase, while the initial oxidation state in the aqueous solution was pentavalent. Rapid reduction of Np(V) to Np(IV) occurred in the presence of hydrogen peroxide and DIDPA.

Experimental results of continuous extraction using mixer-settlers showed that 99% of neptunium in 0.5 M nitric acid feed solution (45°C) was recovered. As a result, DIDPA can extract simultaneously uranium, neptunium, plutonium, americium, and curium from HLLW if the acidity is adjusted to 0.5 M. The back-extraction of Am + Cm, Np(IV) + Pu(IV), and U(VI) can be achieved with 4 M nitric acid, 0.8 M oxalic acid, and 1.5 M sodium carbonate (Na_2CO_3), respectively.

In addition, DIDPA is more tolerant of radiation than TBP and the decomposition products of DIDPA, if present, have negligible effect on the extraction behaviour of the metals.

4.1.1.7 TALSPEAK

The TALSPEAK [157] process extracts lanthanides from trivalent actinides using di(2-ethylhexyl) phosphoric acid (HDEHP) to extract the lanthanides from an aqueous solution of lactic acid and diethylenetriaminepentaacetic acid (DTPA) in the pH range 2.5 to 3.0. In a “reversed” version of the process [158] both lanthanides and trivalent actinides are extracted into HDEHP, followed by selective stripping of the trivalent actinides into an aqueous solution of lactic acid and DTPA. The lanthanides can be stripped from the organic extractant with 6 M nitric acid. Del Cul *et al.* have recently studied the use of citrate as the aqueous phase complexing agent [159].

4.1.1.8 TRAMEX

The TRAMEX process [160-162] was developed to separate transplutonium elements from irradiated High Flux Isotope Reactor targets. In this process trivalent actinides are extracted using a tertiary amine hydrochloride. The aqueous phase is a 10 M LiCl solution containing actinides and fission products. Nickel is the only contaminant that follows the transplutonium elements through the process. No serious radiation effects were noted at activity levels up to 10 W/l. Acid is destroyed at the rate of about 0.1 M per day at radiation levels of 10 W/l. Because the process is affected by small changes in acidity, reducing agents such as methanol and formaldehyde is used to prevent acid loss.

4.1.1.9 Advanced separations

There are many new or advanced processes that have been proposed. A few of the methods that appear promising or that can be applied in special situations are mentioned below.

4.1.1.9.1 Crown ethers

Although solvent extraction on the basis of synergistic effects is useful for the separation of actinide and lanthanide ions having large co-ordination numbers, the selectivities in the mutual separation of those elements so far observed are not sufficiently large. In principle, macrocyclic polyethers such as crown ethers have the advantage that crown ethers complex selectively with a metal ion of ionic size similar to the cavity size of the crown ether molecule. Several studies have been carried out to enhance the selectivity in the separation of lanthanides and actinides in the synergistic extraction system on the basis of the size-fitting effect of the crown ethers [163-165].

Recently, Meguro *et al.* of JAERI found a synergistic ion-pair extraction reaction [166,167] in which actinide(III) and Ln(III) ions are extracted as cationic complexes, $M(TTA)_2CE^+$ where M, TTA, and CE are metal ion, thenoyltrifluoroacetone and crown ether, respectively, into such organic solvents of high dielectric constant as nitrobenzene, instead of the neutral species $M(TTA)_3CE$, in the conventional synergistic solvent extraction system. (It should be noted, however, that nitrobenzene may meet problems with its acceptance because of its toxicity.) The most significant synergistic effect was observed in the extraction with 18-crown-6 (18C6) or dicyclohexano-18C6, reflecting the size-fitting effect of 18C6 derivatives with the metal ions. The separation factor of Am(III) and Cm(III) in the ion-pair extraction of $M(TTA)_2(18C6)^+$ and ClO_4^- was a few times larger than those for the extraction of $M(TTA)_3(18C6)$, which can also be explained on the basis of the size-fitting effect.

4.1.1.9.2 Beta-diketones

Ensor *et al.* [168] demonstrate that extractions with thio-derivatives of β -diketones give good separations of trivalent actinides from lanthanides. However, already-existing separation methods based on redox behaviour of the lighter actinides (thorium through plutonium) are simpler and more efficient, and may limit use of these soft donor extractants to separation of the heavier trivalent actinides. Wade *et al.* have discussed the application of soft donor ligands to the separation of trivalent actinides and actinides [169].

4.1.1.9.3 Picolinamides

Cordier and Condamines have reported on the use of picolinamides for the separation of trivalent actinides from trivalent lanthanides. In their work they studied the mechanisms of complexation and extraction using picolinamides, and found factors that improved extraction, as well as ways to improve the stability of picolinamide in acid media [170].

4.1.1.9.4 Diphosphonic acids

Substituted diphosphonic acids have been studied for their application in solvent extraction separations of metal ions, including tri-, tetra-, and hexavalent actinide ions [171]. There is an extraordinarily strong affinity for the tetra- and hexavalent actinide ions. Extraction of tetra- and hexavalent actinides is almost independent of acid concentration. However, there is a strong dependence on acidity of the aqueous phase for trivalent actinide extraction.

4.1.1.9.5 Calixarenes

Calixarenes [172,173] are organic molecules based on cyclophane backbones that contain cavities such that they resemble molecular-size baskets. They are formed in reactions using alkali salts as templates: reaction of aldehydes with para-substituted phenols or with resorcinol yields calixarenes or resorcinarenes, respectively. Because of their basket-like nature calixarenes are capable of encapsulating ions or smaller molecules and shielding them from solvent molecules. By careful control of the conditions of synthesis calixarenes can be tailored to accommodate selectively a variety of metal ions or organic molecules. For example, alkali ion-selective calixcrowns are formed when crown ethers are incorporated into calixarenes [174]. Although not yet in practical use for the separation of actinides from wastes, calixarenes have the potential for this application.

4.1.1.9.6 TPTZ

Tripyridyltriazine (TPTZ) is a terdentate nitrogen-donor ligand which can selectively extract An(III) from actinide and lanthanide mixtures when used in synergistic combination with an organic cation exchanger. This system was first studied in the 1980s by Vitorge [175]. Good separation factors were obtained for An(III) vs. Ln(III) using TPTZ + HDNNS (di-nonylnaphtalenesulfonic acid) or TPTZ + alpha-bromocaproic acid. Tests of the process using synthetic spiked solutions were successfully conducted at Fontenay-aux-Roses [176-179]. Improvements to the process are underway in a European research programme. One way to improve the system is to use the lipophilic alkyl derivative of TPTZ developed jointly by the University of Reading, UK and the CEA, France [180]. With this improved system, An(III)/Ln(III) separation can be expected from 0.1 to 0.2 M aqueous nitric acid solutions.

4.1.1.9.7 SESAME process

It has been known for some time that the existence of americium in oxidation states higher than 3+ can be exploited to design americium separation processes from lanthanide and/or curium. The so-called SESAME process is based on Russian works [181] and is being developed at CEA Marcoule, France [182-190]. The process is based on the use of heteropolyanions (HPAs), such as phosphotungstate $P_2W_{17}O_{61}^{10-}$, which allow the oxidation of americium to Am(IV), for example by electrochemical means, due to the extraordinary complexing power of HPAs for An(IV) species. If the HPA/Am ratio is lower than 0.5, the Am(IV) complexed with the HPA disproportionates, leading finally to ~100% of non-complexed Am(VI). Several alternatives are available for designing SESAME processes. They can be based on the extraction of either Am(IV)/HPA complexes or of Am(VI). Tests of the process are currently underway at Marcoule, France. The SESAME process is also being investigated by Kamoshida [191].

4.1.2 Precipitation

Precipitation is the oldest large-scale technique employed for separating actinides. The earliest uranium separations were based on precipitation of "diuranates" and hydroxides from acid solutions [192]. This resulted in a quite impure and complex product [193]. Later, more selective precipitation processes employing oxalates, carbonates, peroxides and fluorides were employed. The first large-scale separation of plutonium employed co-precipitation of plutonium with bismuth phosphate [192,195].

When precipitating the higher-valent, non-oxygenated actinides and lanthanides, care must be taken to prevent colloid formation at higher pHs. Plutonium(IV), thorium and uranium are especially susceptible to colloid formation [196], to the extent that nuclear fuel production methods have been developed based on the formation and subsequent gelation of their colloids [50,197].

The IAEA prepared a comprehensive and useful document on chemical precipitation processes for treating aqueous radioactive waste [198].

4.1.2.1 Actinide compounds

Oxalates, carbonates, peroxides and fluorides have been especially useful precipitants for actinides because they are quite selective under the proper conditions of pH and concentration, and the purified precipitates they form may be used to produce the pure oxides or the metals.

4.1.2.1.1 Oxalate

The insoluble oxalate of Pu(IV) is widely used as a precursor of the PuO₂ feed material in the preparation of plutonium-containing fuel [199]. Upon thermal decomposition it produces a pure but very finely divided oxide powder. Oxalate precipitation has also been used to purify Am(IV) by selective precipitation of lanthanides [200] from solution and to prepare neptunium oxide through precipitation of the oxalate followed by calcination [201].

4.1.2.1.2 Carbonate

Although alkaline carbonate solutions form strong tricarbonates complexes with uranium, ammonium uranyl tr carbonate is relatively insoluble, and is used in the commercial preparation of nuclear reactor fuel. Alkali metal uranyl tr carbonate has also been shown to co-precipitate with Np(V), Pu(V), and Am(V) [1,202].

4.1.2.1.3 Peroxide

The actinide elements uranium, plutonium, neptunium and thorium all form insoluble peroxides [203,204]. The peroxides are precipitated from dilute acid solution with hydrogen peroxide. Acidic peroxide solutions have long been used to produce pure hydrated uranium and plutonium peroxide products. Although the precipitation is not quantitative, the yield is acceptable, and products are pure enough for direct use in the preparation of the metals for weapons manufacture or fuel preparation.

4.1.2.1.4 Fluorides

Fluoride precipitation has found use in the separation of tri- and tetravalent actinides, and may still be of use when an inorganic precipitant is sought. In general the fluoride precipitate is granular and easily handled. (The metals are readily prepared in pure form from the fluorides by reduction with active metals such as calcium.)

4.1.2.1.5 Uranates

Uranium forms a series of hydrated oxides and hydroxides [205]. In addition, it forms families of uranates and diuranates. In the uranates the uranium is present along with another cation in compounds of the general composition $M_2U_xO_{3x+1}$, where M is a monovalent cation. Uranates are also formed with divalent cations such as calcium and magnesium. Ammonium diuranate is of particular interest because of its commercial use in reactor fuel preparation. The addition of ammonium hydroxide to aqueous solutions of uranyl nitrate produces a precipitate of the so-called ammonium diuranate, a hydrated uranyl hydroxide containing NH_4^+ [206]. This compound is of somewhat uncertain composition, but is generally written with the formula $(NH_4)_2U_2O_7$. It decomposes to form UO_3 below $580^\circ C$, and above to form U_3O_8 . In air U_3O_8 begins to decompose at about $900^\circ C$, but complete conversion to UO_2 is extremely difficult.

4.1.2.1.6 Hydroxides

Precipitation of hydroxides and hydrous oxides is perhaps the oldest method of separating actinides from other species. It is, however, an inefficient purification process because so many other metallic elements form insoluble hydroxides in alkaline solutions. Krot *et al.* [207] discuss the co-precipitation of TRU elements from alkaline media, and Peretrukhin *et al.* [208] report on the precipitation of TRU elements from alkaline solutions. Peretrukhin *et al.* [209] examine the effects of valence changes and of complexing agents on the solubility of TRU elements in NaOH solutions.

4.1.2.1.7 Colloids/pseudocolloids

The hydrolysis of metal cations is of great importance in both basic studies and applications (see the discussion in Section 3.1.1.4). Mesmer and Baes summarised the status of studies of metal cation hydrolysis up to the mid 1970s [210]. Hydrolysis often leads to polymer formation through formation of hydroxyl bridges that convert to oxygen-bridged polymeric (colloidal) species. It is easy to form colloids of plutonium. If acidic solutions of Pu(IV) are allowed to become too basic the colloid (often referred to as plutonium polymer) is formed. If it is allowed to age it becomes quite refractory, and may require vigorous treatment to put it back into ionic form. Plutonium polymer may form locally in solutions where aqueous condensate falls back from a condenser into an acidic solution creating local lower acidity, even though the average acid concentration of the solution is sufficiently high to prevent polymer formation. (This behaviour is of particular importance in separation processes where plutonium recovery depends on retaining plutonium in the ionic state, and in extreme cases can lead to accumulation of plutonium in unexpected places in the process.) Uranyl ion may attach to Th(IV) [211] and Pu(IV) colloids during the formation of the plutonium polymer. Thiyagarajan *et al.* have reported on the formation of plutonium(IV) polymers in aqueous and organic media [212].

4.1.2.2 Co-precipitation

Co-precipitation has been widely used to separate actinides from solutions, especially when they are present in very low concentrations [213]. It employs one of two basically different mechanisms. The minor constituent (the one being carried) may be included in the crystal lattice of the precipitant, or it may be sorbed on the surface of the precipitant. A variant of surface sorption is inclusion in the matrix of an amorphous solid, such as ferric hydroxide. A potential problem with co-precipitation is that in many cases it is not very selective. For example, ferric hydroxide has virtually no selectivity,

and acts as an efficient scavenger of virtually all ions in solution. Another broad spectrum precipitant is manganese dioxide. The quantitative co-precipitation of neptunium, plutonium, and americium with barium sulphate is described by Kimura *et al.* [214].

4.1.2.2.1 Scavenging

Recovery of actinides (and many other elements) by scavenging is a widely used technique. It is particularly effective for the removal of actinides present in relatively low solution concentrations. The most widely used scavengers have ferric hydroxide and manganese dioxide. These materials are quite non-specific in the removal of ions from solutions. Ferric hydroxide is especially prone to indiscriminate scavenging, presumably by incorporation of ions into gelatinous matrix. Manganese dioxide can be formed as a finely divided solid which is more specific in its action. It has been used to remove the fission products zirconium and niobium from the uranium and plutonium products of solvent extraction processes. Sorption of uranyl ion on hydrous silica is discussed by Lieser *et al.* and is compared with sorption on hydrated alumina and titania. Silica gel is used as a final clean-up step for uranyl nitrate solutions. It removes γ -emitting impurities by a factor of about 20.

4.1.2.2.2 Bismuth phosphate

The original separation of plutonium was carried out by co-precipitation with bismuth phosphate. A large-scale process was installed at the AEC Hanford Works in the early 1940s and the first plutonium bomb was prepared from plutonium recovered by this process. The bismuth phosphate was supplanted by the much more efficient solvent extraction processes, and is now largely of historical interest only.

4.1.3 Chromatography

Chromatography is based on the principle of multiplication of single-stage separation factors by arranging the separation medium such that the products of one separation stage directly feed additional stages, thus significantly enhancing the degree of separation obtained. The physical arrangement usually employed is to put the separation medium (typically an ion exchange resin) in a vertical column. The feed solution enters from the top or bottom of the column where it attaches to the exchange sites of the resin. The chromatographic process occurs as the ions to be separated are eluted preferentially through the column with a carefully chosen eluent.

Both organic and inorganic ion exchangers may be used in chromatographic separations as may extraction chromatography in which a liquid separation medium is typically sorbed on a high-surface-area material. The subsequent steps are as described above.

4.1.3.1 Organic ion exchange

Organic ion exchangers have been used since the mid-1940s to separate actinide and lanthanide elements. More recent developments have focused on synthesis of ion exchangers with highly specific functional groups, enhanced radiation resistance, and shorter equilibration times. The functional groups can be easily ionisable cation exchange groups such as sulfonic acid, or less easily ionisable weakly acidic groups, such as carboxylic acid or phenol groups. There are also easily ionisable anion

exchange groups such as tertiary alkyl ammonium and less easily ionisable groups such as di- or trialkyl ammonium groups. Often several types of functions are included in a single resin. The recently developed Diphonix resin is an example of this type of resin [219].

A very large number of actinide separations have been performed using “conventional” organic ion exchangers of the strongly basic anion exchange type [220]. A great many actinide separations are based on anion exchange rather than cation exchange because of the pronounced ability of the higher valence states of the actinides to form anionic complexes, thus facilitating their separation from metal ions which do not form anionic complexes. Trivalent actinides are not at all or only slightly sorbed from aqueous nitric acid and hydrochloric acid solutions. In general, anionic complexes of tetravalent actinides absorb in the increasing order of bonding $U(IV) < Np(IV) < Pu(IV)$ in both nitric and hydrochloric acid solutions. Th(IV) does not appear to bond at all from hydrochloric acid solutions, but does form strongly bonded anionic complexes in strong nitric acid solutions. Sulphuric acid, although less widely used than nitric and hydrochloric acids as a separation medium, does form strongly absorbed anionic complexes with uranium and thorium when it is dilute (less than about 2 M).

Strongly acidic cation exchangers bond strongly with many cations if the acid concentrations are not too high (in general not above about 4 M). Therefore, although actinide separations can be made using these ion exchangers, they do not afford the selectivity for actinides that may be obtained using anion exchangers. Because complexation can interfere with cation absorption by forming anionic species complexation is generally avoided, and the actinides are absorbed in positive valence states. Conversely, cations may be eluted from cation exchange resins using complexing agents that form anionic species with actinide ions.

Both sorption and elution may be used to obtain separations. In the former case the separation is obtained by selective uptake of one ion over another; in the latter, separation is obtained by selective elution of one ion over another. The elution may be carried out with a complexant that preferentially removes one or more ions, or by changing acidity or concentration of the eluent such that sorbed ions are eluted sequentially. An early and classic example of complexant elution is the use of 2-hydroxy-2-methylpropanoic acid (α -hydroxy-isobutyric acid) for separating transplutonium elements [221].

Organic ion exchange resins may be prepared in a variety of physical forms. The form chosen depends upon the intended use. In general, ion exchange resin particles may be classified as (a) conventional, (b) superficial, (c) supported, (d) pellicular and (e) macroporous.

- *Conventional resins* are solid and have functional groups throughout their mass.
- *Superficial resins* have a superficial layer, or skin, of the organic matrix converted into ion exchange resin. They are useful when rapid exchange is more important than capacity.
- *Supported resins* are created by forming ion exchange resin in the cavities of porous carriers such as silica. Very high porosity exchangers with rapid exchange kinetics can be obtained in this way, along with practical ion exchange capacities.
- *Pellicular resins* are formed by coating “inert” support microspheres with a layer of ion exchange resin. Thus, they have properties that are generally similar to those of superficial resins. In fact, the support material may contribute to the ion exchange properties.
- *Macroporous resins* which are similar in some ways to supported resins, are discussed separately below.

4.1.3.1.1 Macroporous resins

Conventional organic ion exchange resins typically are made of an organic matrix with functional groups attached uniformly throughout the bead. The organic matrix is hydrophobic and it is the ionisable functional groups that facilitate suffusion of water throughout the gel. Macroporous ion exchangers are beads made with interconnected porosity, similar in appearance to a tiny sponge. The aqueous medium fills the pores, and the distance from the aqueous phase to the functional (exchange) groups is greatly shortened. This can very greatly shorten the equilibration time. A macroporous bifunctional phosphinic acid resin that can be loaded over a wide range of acidity and eluted easily with a dilute ammonium carbonate solution was described by Sabharwal and Rao [222] for uranium recovery from a variety of media.

4.1.3.1.2 Radiation resistant resins

The radioactivity of the actinides and of the solutions that are present with them in process streams and wastes poses a significant radiation problem for the organic ion exchange resins frequently used in separation of the actinides. Although there have been hundreds of types of ion exchange resins synthesised, the number that have achieved industrial importance is much smaller. These generally fall into a relatively small number of types which include copolymers of styrene and divinylbenzene with cation or anion exchange functional groups, polyvinylpyridine anion exchangers, chelating resins and multifunctional resins.

Pillay provides a comprehensive survey of effects of ionising radiation on synthetic organic ion exchangers [223], and Marsh and Pillay supply an up-to-date review of the very extensive literature on the subject [224].

The radiation resistance of ion exchange resins is affected by degree of cross linkage (higher cross linking decreases radiation effects), moisture content, the salt form in which they are present (anion exchangers in the nitrate form are generally more stable than those in the chloride form; the hydroxide form is the least stable), and the chemical nature of the surrounding medium. In general, strong-acid cation exchange resins are more resistant to radiation than strong-base anion resins, and polyvinylpyridine resins are more resistant than polystyrene resins. Gamma radiation is more damaging than *in situ* α radiation at the same absorbed dose. Radiation doses in the range of 10^5 Gy* alter the properties of most synthetic organic ion exchangers.

Reillex™ HPQ, a copolymer of 1-methyl-4-vinylpyridine and divinylbenzene, is a macroporous anion exchange resin that shows great resistance to radiation and chemical attack. It is more resistant to both γ and α radiation than any of a wide range of organic ion exchangers at doses up to 10^4 Gy.

Practical effects of irradiation on strong acid (sulfonic acid) resins was obtained in the TMI-2 EPICOR-II Resin/Liner Investigation: Low-Level Waste Database Development Investigation [225]. In this investigation it was found that substantial loss of ion exchange capacity occurred at about 5×10^5 Gy (5×10^7 rad); at 1.5×10^6 Gy (1.5×10^8 rad) the capacity loss was equal to or greater than 50%. This is lower than the recommended dose limit [226]. However, it was found to be very difficult to remove sorbed ions from the irradiated resin even at high losses in exchange capacity because the degraded resin agglomerated in the bed, greatly restricting the flow of water through it.

* Gy is the symbol for Gray, the SI unit of absorbed dose. 1 Gy = 1 Joule/kg = 100 rad

4.1.3.1.3 Multifunctional chelating resins

The recently developed Diphonix™ resin exemplifies multifunctional chelating resins. It contains geminally substituted diphosphonic acid ligands chemically bonded to a polystyrene-sulfonic acid matrix. Diphonix resin exhibits an extraordinarily strong affinity for actinides in the tetra- and hexavalent oxidation states. The sulfonic acid cation exchange group enhances rapid access of ions into the otherwise hydrophobic polymer matrix. The diphosphonic acid group provides the specificity for specific cations. Diphonix resin can be grafted to a silica support [227] to produce a resin that may be well suited to fixation of actinides in a form that may be considered for use as a final waste form.

4.1.3.2 Extraction chromatography

Extraction chromatography combines the favourable characteristics of solvent extraction and ion exchange. It involves impregnating a porous granular material with a liquid that can selectively extract chemical species of interest from solutions containing a mixture of chemical species. The granular material is placed in a column and separations are carried out in much the same way as in ion exchange, except that solvent extraction rather than ion exchange is the effective separation process. Despite the limited capacity of the reagent-loaded material, extraction chromatography is very promising, especially for the decontamination of fairly small quantities of actinide elements in liquid radioactive wastes. Extraction chromatographic methods with TBP [228-231] and DHDECMP [232-235] have been extensively applied to the separation of actinides in nitric acid media. The extraction chromatographic behaviours of various actinides were studied in comparison with those in the much more widely used conventional solvent extraction systems.

4.1.3.2.1 CMP and CMPO

CMP and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO), bifunctional organophosphorus compounds which show high selectivity in the extraction of actinides and lanthanides from nitric acid, have been employed for the stationary phase in extraction chromatography [236].

Distribution coefficients of Am(III), Pu(IV) and U(VI) were measured between nitric acid and TBP + CMP/XAD-4 or TBP + CMPO/XAD-4 resins, indicating that extraction chromatography using these resins are more effective than conventional ion exchange resins for removing actinides from nitric acid solutions. The results of the elution behaviour of Np(V), Am(III), Cm(III) and fission products with CMP/XAD-4 showed that Np(V) and fission products, except lanthanides, were effectively separated from trivalent actinides and lanthanides using only nitric acid as eluent.

Chromatographic extraction with CMPO has been shown to be effective for the separation of minor actinides from PUREX high-level waste [237]. A system comprising CMPO sorbed on chromosorb-102 was shown to have a high uptake of both actinides and lanthanides from 0.5 to 6.0 M nitric acid.

4.1.3.2.2 Hollow fibre

An adaptation of extraction chromatography involves the use of porous, hollow fibres [238] as the sorption medium. This adaptation offers several advantages over columns packed with liquid-extractant impregnated granules. First, the pressure drop is typically much less in a hollow fibre

system than in a column system; second, it is generally easier and therefore less costly to produce uniform hollow fibres than it is to produce uniform particulate materials. There are two practical geometries for hollow fibre systems. The first, and most common geometry is a bundle of hollow fibres arranged so that a stationary phase impregnated in the porous hollow fibre is contacted with a mobile phase containing the species to be separated [239]. Typically, the mobile phase is introduced into the hollow core of the fibre and selective sorption occurs as the mobile phase passes through the wall of the fibre in a manner similar to elution chromatography. The second geometry is a shallow packed bed of hollow fibres similar to a very thin bed of very large cross-sectional area.

Fibres are typically made of microporous polypropylene having diameters in the range of 100 to 400 microns. Any of a large number of liquids may be sorbed in the pores of the fibres, depending on the separation sought.

4.1.3.3 Continuous annular chromatography

A novel variation on chromatographic separations may be found in what is called the continuous annular chromatography (CAC) [240]. While chromatographic separations almost always are carried out batchwise, CAC employs continuous feed and separation of several species simultaneously. The innovation is embodied in equipment that permits continuous feed and separation of chemical species on an apparatus consisting of an annular bed of adsorbent particles. The apparatus is rotated slowly about its axis while eluent and feed solution are fed into one end of the bed. Eluent is fed to the entire bed circumference while the feed mixture is introduced into a narrow sector of the circumference at a single point. Helical component bands develop with the passage of time extending from the feed point, with slopes dependent on eluent velocity, rotational speed, and the distribution coefficient of the component between the fluid and sorbent phases. The separated components are continuously recovered once steady state is attained as they emerge from the annular column, each at its unique position on the circumference of the annular bed opposite the feed end. Separations can be carried out with simple or gradient elution, wherein the eluent concentration is changed continuously.

4.1.3.4 Biosorption

A variety of biomass materials have been studied for their potential applications for recovery of metals from process streams or liquid wastes [241,242]. These include bacteria, algae, yeast and fungi. Microbial biomass in its natural form is not generally suitable for large scale process use because of its small particle size, low mechanical strength and relatively low density. Immobilised biomass does not have these limitations, and has potential for use in packed or fluidised bed reactors [243].

An example of biosorption is the sorption of uranium on *pseudomonas aeruginosa* strain CSU. Uranium loading behaviour could be described by the Langmuir isotherm. Uranium loading was pH dependent, increasing with pH under acidic conditions. Preliminary evidence suggests bonding of both anions and cations. Live, dead, permeabilised and unreconstituted lyophilised cells were all capable of binding uranium. Ferric ion was a strong inhibitor of uranium binding, and should be removed from waste solution before treatment to remove uranium. At less than saturation loadings of Fe^{3+} , uranium interfered with iron loading.

Maximum uranium loadings of about 100 mg/g (dry weight) were obtained from solution containing uranium in the range 10 to 100 ppm. In addition to ferric ion, other ions such as Cu(II), Pb(II), Cr(III), and Al(III) interfered to some extent (about 50 to 75% reduction in uranium loading).

4.1.3.5 Inorganic ion exchange

Inorganic ion exchangers [244-247] find application where resistance to radiation, heat or chemical attack is important. They also have special applications where extreme selectivity is needed, or where they incorporate wastes in a material that might be suitable as a final waste disposal form. Inorganic exchangers are found in nature as natural zeolites and clays. They may also be synthetic zeolites, oxides and hydrous oxides, acidic salts of multivalent elements and cyanoferrates [248]. After an extensive review of the literature by Hooper [249], hydrous titanium oxide, manganese dioxide, titanium and zirconium phosphates, polyantimonic acid and copper hexacyanoferrate were selected for experimental evaluation. More recently Brown and colleagues have developed and brought to commercial availability a class of crystalline silicotitanates (CSTs) whose properties can be tailored to be selective for specific cations. These inorganic systems are at present finding more applications to separations of fission products than to separations of actinides.

Inorganic ion exchangers have often been difficult to prepare in a practical form such as beads for use in a column because they are usually powders, and require a binder to hold the powder particles together. Both the exchangers and the binders are often not stable across a wide range of pH, and may be limited to either an acidic or a basic medium, but not both.

4.1.3.5.1 "Inclusion" exchangers

Inorganic ion exchangers may operate functionally either by sorption from aqueous solutions of ions on surface sites or by trapping ions in zeolitic cages whose size and ionic charge play a role in ion selectivity. In the latter case great ion selectivity is often achieved. Aluminosilicates, which show great promise for selectively exchanging ions out of aqueous media, are discussed by Qureshi and Varshney [250]. Crystalline aluminosilicates show extremely high selectivity for caesium, and show promise for application to separation of other ions [251].

Aluminosilicates (zeolites) constitute the largest group of inorganic ion exchangers. Replacement of tetravalent silicon ions with ions of lower charge, e.g. trivalent aluminium ions, and aluminium ions by divalent ions, e.g. magnesium or Fe^{2+} , leads to a net charge on the zeolite lattice that is compensated by electrostatically bound alkali or alkaline earth metal cations. These cations are mobile, and are subject to ion exchange with ions in a surrounding solution. The ion exchange is, however, limited by the three-dimensional structure and dimensions of the lattice spacing in the zeolite. "Windows" and channels exist in the zeolite and cause it to exhibit selectivity for ions of appropriate size, while excluding ions that are too large to enter the zeolite. In addition to ion exchange, purely physical sorption can occur on zeolites. In this case ions are bound to the zeolite by weak attractive forces, often called van der Waals forces, to the charged zeolite surface.

In addition to aluminosilicate ion exchangers, there are hydrous oxides, acidic salts of multivalent metals, salts of heteropolyacids and insoluble ferrocyanides that can react with and exchange ions. Insoluble ferrocyanides in particular have found wide application in radiochemical separations because of their high selectivity and good chemical and mechanical properties.

Zeolites can be prepared in both amorphous and crystalline forms. Crystalline exchangers, because of their ion-sieve properties, can be used to carry out very good separations of inorganic ions of different radii. However, because of the formation of new crystalline phases and hysteresis phenomena in the crystalline zeolites, amorphous exchangers are sometimes preferred. Many metals and anions have been used to form amorphous exchangers. The metals include aluminium, antimony,

bismuth, cerium, chromium, cobalt, iron, lead, magnesium, niobium, tin, tantalum, titanium, thorium, tungsten, uranium and zirconium. Anionic species include phosphate, tungstate, molybdate, arsenate, antimonate, silicate, telluride, tellurite, ferrocyanide, vanadate, arsenophosphate, arsenotungstate, arsenomolybdate, phosphomolybdate, phosphovanadate, molybdosilicate and vanadosilicate.

Separation of Am^{3+} and Cm^{3+} mixtures was carried out on amorphous zirconium phosphate, whereon Am^{3+} is converted to AmO_2^+ . This phosphate was also used to separate plutonium from uranium and fission products in a solution of 0.5 M nitric acid and 0.02 M sodium nitrate (NaNO_3). A decontamination factor of approximately 1×10^3 was found for UO_2^{2+} over the temperature range 20-30°C.

4.1.3.5.2 Matrix supported

A variety of physical structures have been examined to support inorganic exchangers, including inorganic binders and various glass fibre and organic polymeric matrices. Use of matrix supports can circumvent the need for binders, which may dilute the exchanger and add bulk to the exchangers when they are finally disposed of as waste. The matrix supports may be fabricated into a variety of forms, one of the more useful being cartridges that can be installed in the same containers as are used for filters [252].

4.1.4 Membrane techniques

Membranes have found extensive use in separations, both as sheets and in a variety of tubular or hollow fibre forms. They have also been used for the electrolytic destruction of ions such as nitrate and nitrite [253]. They may function by ion exchange, by extraction, or by exclusion of ions or molecules. Recent developments have greatly extended membrane types and applications to include inorganic membranes, supported liquid membranes and polymeric membranes.

4.1.4.1 Supported liquid membranes

Supported liquid membranes (SLMs) are formed when solvent extraction reagents are immobilised on inert, microporous supports. The supports may be either organic or inorganic, and may assume a variety of geometries ranging from beads, to sheets or plates, and to tubes, and may be single or multilayer composites. Danesi discusses organic SLMs and developed models and equations to describe the permeation of metal species through them [254]. Also, Danesi *et al.* outline the separation of 10^{-6} M americium in nitrate solution using CMPO in diethyl benzene supported by a polypropylene film [255]. Actinides were separated from as many as 40 metal species using this technique. Membrane instabilities can result from loss of extractant because of its solubility, increased wetting of the support pores through the action of surfactants such as alkylaryl sulfonic acids and long-chain quaternary alkylammonium salts, and differential pressures between the inside and outside of hollow fibre SLMs. Tavlarides describes the use of inorganic supports for metal ion separations, although not for actinide separations [256].

4.1.4.2 Ion exchange membranes

Ion exchange membranes possess all the advantages of conventional bead ion exchangers with the additional benefit of being in the form of sheets that can be used in several configurations and in numerous applications. They are especially useful where isolation of solutions is sought but ionic conduction is required, as for example in electrolytic cells. Although most ion exchange membranes are organic, there are also inorganic ion exchangers. The latter type are applied where physical strength is especially important or where extremes of chemical, thermal or radiation exposures exist.

4.1.4.2.1 Organic

Organic ion exchanger membranes have found wide industrial use in separations [257], both within the nuclear industry and outside it. Both the chemical and physical nature of the membranes are of great importance when considering specific applications. In addition to the nature of the membrane materials, their configuration in equipment used is important. Typically, organic exchange membranes are of the same composition as particle or bead ion exchangers. Very often they consist of a polystyrene matrix with ion exchanging functional groups attached throughout the matrix.

4.1.4.3 Water-soluble chelating polymers

Water-soluble chelating polymers are polymers specifically designed to bind selectively with metal ions in aqueous solutions [258]. The polymers' molecular weights are high enough that the ions can be separated and concentrated using available ultrafiltration technology. A series of water-soluble chelating polymers has been prepared with functional groups of phosphonic acid, acylpyrazolone and hydroxamic acid. These groups display an affinity for high-valence metal ions such as the actinides in preference to low-valence metal ions such as alkali metals and alkaline earths in acidic nitrate and acidic chloride solutions. The concentration of polymer is typically 1-2%. The ultrafiltration membrane is chosen to have the appropriate molecular weight cut-off, typically with 10-100 μm pores [259]. Phosphonic acid polymers were used to separate americium with good separations from a variety of other metal ions and anions present in much higher concentrations [260]. Iron (III) did not interfere until it reached a concentration of about 1 500 ppm. Separation and preconcentration of actinide elements in trace concentrations using a water-soluble oxine polymer is discussed by Russian and German scientists [261].

A variation of the hollow fibre technique relies upon binding the species whose separation is sought with a high molecular weight polymer. The bound species will not pass or will resist passage through the pores in the fibre, thus effecting separation from those species that do pass through [262]. There are many potentially useful polymers for this type of application [263]. A typical water-soluble chelating polymer is polyacrylic acid which has a molecular weight of about 90 000. Microporous fibres of polyacrylonitrile having a thickness of 0.3 mm, a length of one or two meters, and an inner diameter of 0.8 mm are typical. More conventional semi-permeable membranes such as those used in reverse osmosis, e.g. cellophane, may also be used.

4.1.5 Dissolution/leaching

In general many operations in the nuclear fuel cycle result in the creation of radioactively contaminated surfaces that cause problems either because of the resultant radiation levels or because of contamination with α -emitters such that TRU wastes are produced, complicating waste disposal.

In most cases it is possible to remove such surface contamination by chemical or physical means, or a combination of both. An example of such a contaminated surface occurs with spent fuel cladding, where actinides (mostly plutonium) are both on the superficial inner layer of the cladding because of sorption, and in the cladding because of atomic recoil reactions. Another example is with ceramic crucibles used in the preparation of plutonium metal where plutonium penetrates the crucible wall and is retained. While the amount of plutonium retained in both of the above examples is relatively small, it is not negligible from the point of view of waste stream treatment.

4.1.5.1 Spent fuel decladding

The recycling of irradiated nuclear fuels usually involves the mechanical subdivision of the fuel elements or fuel element bundles. The principal decladding methods are chemical, mechanical or combined decladding [264]. The chemical decladding processes are subdivided into wet chemical decladding and oxidative decladding [265]. In wet chemical decladding nitric acid is used to dissolve the fuel, leaving the cladding behind. Vest prepared a literature review of the decladding of Zircaloy-clad LWR fuel [266].

4.1.5.1.1 Distribution of actinides

Reactor fuel claddings typically are made of Zircaloy (light and heavy water reactors) and stainless steel (fast reactors). There are three principal types of radioactivity associated with cladding: activation products, fission products and actinides. The amounts of actinides depend on the quantities of unremoved fuel and, to a lesser extent, on other effects such as deposition on the surface during the decladding process or implantation in the cladding as a result of atomic recoil. For short cooling times the main source of radioactivity is from neutron activation, but as these activities decay to relatively low levels (from 100 to 500 years) the major residual activities are due to contamination from the fuel itself and from other actinides.

Measurements of the total fissile content of stainless steel hulls, calculated assuming that all the activity is due to ^{239}Pu , varied in the range of 50 to 5 500 μg of ^{239}Pu per gram of hulls. Alpha spectra of the hull surfaces showed very little penetration of the clad surfaces by α -emitters. The measurement technique employed can give information on penetration depths of up to 8 μm ; in most cases the 95% of the α -activity was present in the first 2 μm of the cladding surface, with most being present on the surface [267]. The actinide content of Phoenix FBR fuel hulls was 686 MBq per gram of hull [268].

The accumulation of α -emitters in Zircaloy hulls measured after dissolution of the fuel in nitric acid was increased by fuel burn-up [269,270]. Whereas about 10% of the activity in the interior of the fuel was from natural uranium, about 75% of the α -emitters in the PWR hulls may be attributed to plutonium. The plutonium content of the spent fuel prior to reprocessing was about 0.2% [271]. The enhanced accumulation of α -emitters on the inner surface appeared to be caused by the sorption and/or adhesion of fuel and the oxidation of the inner surface during dissolution of the fuel [267].

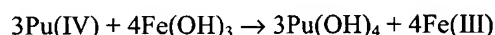
4.1.5.1.2 Decontamination of stainless steel hulls

The effect of nitric acid concentration on the decontamination of DFR (Dounreay Fast Reactor) and PFR hulls [272] by simple refluxing is shown in Table 4.1. The best removals of actinides were obtained with relatively high acid concentrations. The amount of Pu(IV) sorbed during the dissolution

Table 4.1 Decontamination of stainless steel cladding by refluxing with nitric acid

Acid concentration	Per cent removal	
	DFR (for 1 hr.)	PFR (for 2 hrs.)
1 M	77-88	
2 M		46.3-73.2
3 M	89-97	
6 M		89.5-94.7
9 M	98-99	98.7-99.7
12 M		99.6-99.7

step depends markedly on acidity and increases with decreasing acidity. Haissinsky and Paiss [273] suggest that in the case of stainless steel the presence of an oxide film can give rise to the following reaction:



In general, the more corrosive the reagent the more effectively the hulls are decontaminated. Corrosion of stainless steel hulls by oxalic acid or ammonium oxalate can be reduced by the use of hydrogen peroxide as an inhibitor. With such reagents greater than 95% of the actinides can be removed in six hours of refluxing. "Mersevey" type reagents were tried for decontaminating hulls (see Table 4.2 [272]). The unbuffered, lower pH solutions appeared to be more effective, but were slightly more corrosive. The Meservey type reagents were capable of giving good removal of actinides.

Table 4.2 Decontamination of stainless steel cladding with Mersevey-type reagents at 95°C for two hours [272]

Reagent	Per cent removal
0.4 M oxalate - 0.16 M ammonium citrate - 0.34 M H ₂ O ₂ , pH 4	93.1-93.2
0.4 M oxalate - 0.16 M ammonium citrate - 0.1 M NH ₄ F - 0.34 M H ₂ O ₂ , pH 4	94.1
0.4 M oxalic acid - 0.1 M NH ₄ F - 1 M H ₂ O ₂	97.6
0.4 M oxalic acid - 0.1 M NH ₄ F - 0.2 M H ₂ O ₂	98.8

4.1.5.1.3 Decontamination of Zircaloy hulls

The decontamination methods examined for the PWR hulls gave residual actinide activities in the range 4 to 19 MBq/kg of hulls (in obsolete units; 0.1~0.5 mCi/g hulls) [270,273]. These specific activities are not far from the limit of 3.7 MBq/kg of hulls (100 nCi/g of hulls) which defines non-TRU wastes [274,275]. The use of complexing agents of a (cold) corrosive mixture such as 3 M nitric acid with 0.5 M hydrofluoric acid (HF) was not as effective for Zircaloy hulls as it was for stainless steel hulls. This was probably because much of the radioactivity was associated with surface coatings of zirconia.

The gross α activities remaining in the PWR hulls after their decontamination with 6 M nitric acid solution have been measured both for mechanical decladding and oxidative decladding. As shown in Table 4.3 the extent of decontamination of α activity on the mechanically declad hulls was about 98.6%, which is to be expected from the results of other reports [270], the removal of activity from the oxidised hulls was about 94.4%. This means that actinides deposited on the internal surface of the cladding penetrated more deeply into the hulls during their oxidation. Table 4.3 indicates that the degrees of decontamination of actinides from mechanically declad hulls have a tendency to depend on the specific actinides, and that it should be more difficult to remove plutonium from the oxidised hulls than to remove minor actinides.

Table 4.3. Per cent decontamination of α -emitters by 6 M nitric acid [270]

α -emitter	Per cent	Decontamination
	Un-oxidised cladding	Oxidised cladding
$^{239}\text{Pu}/^{240}\text{Pu}$	98.9	91.4
$^{238}\text{Pu}/^{241}\text{Am}$	99.1	94.6
^{243}Am	>99.0	>99.0
$^{242}\text{Cm}/^{244}\text{Cm}$	98.9	99.0
Total	99.0	95.6

4.1.5.2 Refractory materials

A large number of waste materials are in the form of refractory (hard to dissolve) materials. Fluorination of refractory materials is a method that may be used to selectively remove uranium and plutonium from refractory matrices by forming the volatile compounds $\text{UF}_6(\text{g})$ and $\text{PuF}_6(\text{g})$. It has been reported that americium also forms a hexafluoride that shows appreciable volatility [276], but quantitative studies are lacking. Strong oxidising and reducing agents have been suggested as well as complexants to remove the actinides.

In addition, soils and concrete are sometimes contaminated with actinides. As nuclear facilities are retired from service, the quantity of these types of materials will increase greatly. A large number of chemical and physical treatments have been proposed for removing actinides from refractory matrices. These range from volatilisation to aggressive dissolution using reagents such as nitric acid/sulphuric acid [277]. Brewer *et al.* [278] reported on the feasibility of a dissolution process using 5 M nitric acid for aluminium and zirconium types of calcined wastes produced during operation of the US DOE fuel reprocessing plant at Idaho Falls, Idaho.

4.1.6 Supercritical fluid extraction

Supercritical fluid extraction (SFE) is an extraction process wherein the solvent is used under conditions above its critical point. Typically the solvent is held at a temperature close to the critical temperature to enable attainment of as high a solvent density as practicable. This significantly enhances its solvent power. The high diffusibility in the supercritical phase is one of the attractive properties of SFE, making it a potential candidate for the separation or the recovery of metals from solid materials.

SFE has been widely used in industry [279], and recent work has shown considerable promise for environmental clean-up of organic pollutants. Until recently, however, SFE has not been much considered for clean-up of soils or other materials contaminated with actinides. This is because the actinides found in the environment are typically ionic in nature (with the important exception of plutonium, which may be plutonium polymer), and the supercritical fluids employed typically have little solvent power for ions. Many common substances have critical temperatures near ambient, making them relatively easy to use. An important exception is water, which despite its high critical temperature (374.2°C) and critical pressure (22.05 MPa) has potential applications in some types of radioactivity clean-up. More usual substances include carbon dioxide, ethylene, ethane, fluoroform and sulphur hexafluoride. Carbon dioxide, which has a critical temperature of 31.1°C and a critical pressure of 7.38 MPa is by far the most studied substance because it is environmentally benign, non-toxic, relatively inexpensive and easy to handle. Typically, co-solvents such as methanol have been employed to enhance extraction of polar materials.

Recent work [280] shows that by addition of negatively charged ligands to complex the positively charged actinides they too may be extracted. Supercritical extractions of greater than 90% of thorium and uranium (as uranyl ion) from sand and water have been shown to be feasible using supercritical carbon dioxide along with fluorinated β -diketones and TBP added to synergise the extraction. In the case of extraction from soils, organic matter content, pH and moisture are important parameters to consider.

4.1.6.1 Supercritical CO₂ fluid extraction

A large amount of liquid waste from used organic solvent is generated from conventional solvent-extraction process used in fuel reprocessing. The best example of such a solvent is TBP used in the PUREX process. Supercritical CO₂ has been suggested as a potential substitute extraction medium because it has the potential of minimising the amount of solvent waste. Extracted substances can be separated from CO₂ by phase separation by decreasing the temperature and pressure. In addition, CO₂ has other attractive properties such as having moderate critical constants, being available in purified form, easily recyclable, non-toxic, stable chemically and radiochemically, and being relatively inexpensive. There have been only a few studies on supercritical fluid extraction (SFE) of metals, despite potential advantages such as those mentioned above, particularly in applications to the nuclear field.

Recently, Wai and colleagues at the University of Idaho demonstrated [280-282] that metal ions such as uranium, thorium and lanthanide ions in solid materials as well as in aqueous solutions can be extracted by supercritical CO₂ containing various chelating agents, e.g. β -diketone derivatives. Yoshida *et al.* of JAERI also reported [283] that uranium(VI) in nitric acid solution of high concentration can be extracted efficiently with supercritical CO₂ containing a small fraction of TBP. These results indicate that the SFE method may hold promise for application to separation processes in the field of nuclear waste management where a large quantity of radioactive material is handled.

Further investigations are required for a critical evaluation of the applicability of the SFE method. The investigations may involve optimisation of the extraction conditions and evaluation of the compatibility of the SFE procedure under fairly high pressure (15 to 35 MPa) with practical separation processes. To optimise the extraction conditions, extraction behaviour of metal ions of interest should be studied employing chelating agents of various types instead of conventional extractants, e.g. TBP. From a more fundamental point of view, the following thermodynamic and kinetic data are necessary:

- distribution coefficients of metal ions between aqueous solutions or solid phases and supercritical CO₂;
- measurements of solubilities of various metal-agent complexes in the supercritical phase;
- kinetic parameters of the phase distribution of the metals;
- diffusibility of various species in the supercritical CO₂ phase.

4.1.6.2 Decontamination

Lin and colleagues demonstrated [280-282] that U(VI), Th(IV), and Ln(III) sorbed on solid materials such as a cellulose or sand matrixes were extracted efficiently into supercritical CO₂ containing appropriate complexing agents, e.g. fluorinated β -diketone, or binary mixtures of synergistic reagents such as TBP and β -diketone. These results imply that this extraction method may offer a host of applications to the selective separation of actinides and lanthanides for the decontamination of these radionuclides from contaminated solid materials.

4.1.6.3 Metal hydroxides or oxides precipitation in supercritical H₂O

It has been seen [284] that metal ions such as aluminium, iron, nickel, cobalt, zirconium and molybdenum in aqueous solutions precipitated as effectively as their hydroxides and/or oxides when the aqueous solution was at supercritical conditions. This behaviour is attributed to the enhancement of the dehydration and hydrolytic reactions of aqueous metal ions and the polymerisation of the hydroxides in supercritical H₂O. This precipitating reaction is attractive as an alternative separation method based on the precipitation or co-precipitation of radionuclides in contaminated aqueous waste such as HLLW, because this novel technique does not require the addition of other chemicals for the neutralisation of the medium or for the formation of a metal-salt precipitate.

4.1.7 Electrolytic techniques

The use of electrolytic processes in separations in the aqueous phase is relatively new in waste stream treatment, although substantial literature exists on the topic of pyrochemical separations. Some work in aqueous systems has been done in the area of fission product separation, and there have been a few applications to actinide elements. In general, electrolytically assisted processes rely on valence changes of ions to change the chemistry of the element in such a way as to facilitate its elution from an ion exchange resin or to alter its solvent extraction behaviour. Sometimes the valence of another ion is changed and that ion becomes the reactive agent which produces the desired chemical change in the element whose changed behaviour is sought. This is the situation when U(IV) is used as a reductant of plutonium in the PUREX process [144,285].

4.1.7.1 Membranes

In neutralised radioactive tank wastes an important goal is to separate the radionuclides from non-radioactive components. This not only substantially reduces the volume of high-level waste to be stored, but also simplifies separation process. Actinides are destined to be in the high-level wastes from most radioactive tank waste treatment processes. Therefore it is advantageous to separate the

large bulk of sodium salts (typically nitrates, nitrites, and caustic) from the wastes. This may be accomplished by electrochemical salt splitting using inorganic ceramic membranes [286,287]. In this process waste is added to the anode side of an electrochemical cell and an electrical potential drives sodium through the membrane while most other cations are rejected. The normal products of electrolysis in aqueous media are hydrogen and oxygen. Membrane materials are customarily of a family of minerals having the representative composition $\text{Na}_{1-x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$. Substitution of other elements for the zirconium and phosphorous may be made without compromising the crystal structure, although such substitutions can lead to small dimensional changes that may have important effects on transport properties through the membrane. Electrodialysis through organic ion exchangers of aqueous NaCl and KCl solutions containing actinides may be used to precipitate the actinides and recycle the chloride ions as hydrochloric acid. This process has been investigated to remove plutonium from solutions obtained by dissolving spent molten salt residues associated with molten salt extraction of plutonium from americium [288].

4.1.7.2 Assisted processes

An important example of an electrolytically assisted process is replacement of the conventional chemical reduction of plutonium to strip it from TBP in the PUREX process by electrolytic reduction of U(VI) to U(IV) which in turn reduces the extracted Pu(IV) to readily stripped Pu(III) [289]. Another example is electrolytically assisted dissolution of refractory plutonium oxide through the production of Ag(II) or Ce(IV) which in turn rapidly attack the oxide.

4.1.7.2.1 Dissolution – CEPD

Plutonium dioxide is among the most difficult of the actinide oxides to dissolve. This is reflected in the Gibbs energy of dissolution in acidic, non-complexing media ($\Delta G^\circ_f = 32.04 \text{ kJ/mol}$ [290]). It is often necessary to recycle an undissolved fraction of the PuO_2 back into the dissolution step. In the past the most commonly used process to dissolve PuO_2 has been dissolution in boiling nitric acid with a few tenths of a per cent of hydrofluoric acid (HF) added. While this method is indeed effective, it produces a corrosive solution, leading to containment problems. Homogeneous mixtures or solid solutions of UO_2/PuO_2 are more easily dissolved than pure PuO_2 in nitric acid, but regions of non-homogeneity can lead to undissolved PuO_2 . Research and development in the US and France have led to processes for PuO_2 dissolution based on the use of strong oxidants like Ag(II), Ce(IV), and Co(III) [291-293]. Excellent results were obtained with Ag(II), even at room temperature. The Ag(II) is generated electrochemically, and this is the rate limiting step.

The CEPD [294] process using Ag(II) has been implemented in the UP2 800 plant at La Hague. The CEPD process can also be used to recover plutonium from incinerator ash with a yield of at least 98%; metallic and organic wastes have been processed at pilot scale in a hot cell facility.

4.1.7.2.2 Ion exchange

Electrodialysis employing cation and anion exchange membranes has found application in the recovery of plutonium from chloride wastes from electrorefining salts. Wedman and Smith [288] reported on the use of a two-stage process for separating plutonium from acidic chloride waste solutions to produce a concentrated plutonium product. The first stage precipitates the actinides; the second stage splits the chloride salts to produce hydrochloric acid and a mixture of sodium and potassium hydroxides. Electrochemical ion exchange may be used to obviate the need for adding

chemical reagents in some ion exchange processes. Hydrogen ions are electrolytically generated *in situ* by electrolytic dissociation of water to produce an alkaline concentrate of the sorbed ion and hydrogen ion on the resin. In an evaluation of this process [295] it was found that packed beds of CS-100 ion exchange resin, and resorcinol formaldehyde and Lewitat DN-KR ion exchange resins gave decontamination factors as high as 10 000 for caesium elution.

4.1.7.2.3 Valence changes – L-L extraction and chromatography

The use of valence change of an intermediate element to bring about the change in valence in the target element has been mentioned for the case of plutonium in the PUREX solvent extraction process, where U(IV) is generated electrolytically and subsequently reduces Pu(IV) to Pu(III). Another example is the extraction of Np(V) by DIDPA, where rapid reduction of Np(V) to Np(IV) occurs in the presence of hydrogen peroxide and DIDPA (see Section 4.1.1.6). The separation of caesium from waste solutions using films of nickel hexacyanoferrate [296] is still under development. In this study the valence state of the iron in the film is changed electrolytically from Fe(II) to Fe(III). Caesium has a high affinity for the reduced form of the film, but very little for the oxidised form. A significant advantage of this approach is that no chemicals need to be added to remove the caesium from the hexacyanoferrate film.

4.2 Pyrochemical processes

The term pyrochemical processes is meant in this report to include volatilisation, liquid-liquid extraction using either immiscible molten metal phases or immiscible molten metal-molten salt phases, electrorefining in non-aqueous media, vacuum distillation, fractional crystallisation, melt refining, zone melting and gas-solid reactions.

Pyrochemical separation processes have found limited applications in actinide separations but have been used on a very large scale in some of those applications. In particular, volatilisation of uranium hexafluoride in a process called “fluoride volatility” has been used on a very large scale for uranium ore refining and for preparation of UF₆ for use in uranium isotope separation. With the exception of fluoride volatility processes, pyrochemical processes have found their greatest use in recycle of plutonium for nuclear weapons manufacture where they are used to remove ²⁴¹Am produced by radioactive decay of ²⁴¹Pu.

For the most part the pyrochemical processes directed toward fuel recycle have been developed to provide greater radiation resistance, be more compact, produce smaller waste volumes and be more proliferation resistant than the universally adopted PUREX process.

In general, pyrochemical separation processes are more difficult to carry out than aqueous separations, do not give large decontamination factors (a notable exception is fluoride volatility), and do not directly produce wastes that can be converted to oxides and vitrified. However, in those cases for which they are well suited, pyrochemical processes offer distinct advantages over aqueous processes.

Pyrochemical separation processes typically are carried out at temperatures well above ambient, commonly above the boiling point of water and often above 500°C. The separations may be driven by chemical, electrical or physical energy. Although many pyrochemical processes for actinide separations have been studied, few have been carried beyond the research and development stage.

Pyrochemical processes often involve either a molten salt or a molten metal phase, or both. Those involving liquid metals usually capitalise on the chemical stability and selective insolubility of intermetallic compounds in the liquid metals. Cadmium, tin, bismuth, zinc and aluminium are among the metals that have been studied for use in such processes.

The nature of the reagents used and the temperatures commonly employed in pyroprocessing often lead to problems with materials of construction for equipment and facilities and to difficult and frequent maintenance problems.

Much of the work done on developing pyroprocessing was carried out quite early in the development of nuclear energy, before the PUREX process (which is based on aqueous systems) was as firmly entrenched as it now is. A survey of early pyroprocessing work is presented in a publication by British authors [297]. In addition there is a good list of references to early work given in a book by Long [298]. More recent discussions of pyroprocesses may be found in a Lawrence Livermore Laboratory report [299] and in a report by Argonne National Laboratory workers [300].

There are a large number of pyrochemical processes and many ways to classify them. Many have been developed in connection with plutonium processing [301]. In the text that follows, whenever a specific name for a process appears, it is described under that name for ease of identification and location in the literature.

4.2.1 Liquid-liquid extraction

Liquid-liquid extraction in aqueous-organic systems finds a close analogy in liquid metal-molten salt systems. It is even possible to consider using the same type of liquid-liquid extraction equipment, although most often in non-aqueous systems batch processes are used.

4.2.1.1 Salt transport

The Salt Transport Process [302] was developed to recycle LMFBR fuel to produce a product of uranium-plutonium-fission product oxides suitable for fabrication into new fuel with substantial proliferation resistance. The term “salt transport” is applied to a purification technique whereby a metallic solute is transferred selectively from one liquid alloy (donor) to another liquid alloy (acceptor) by circulating a molten salt (typically a mixture of chlorides) between the two alloys. The separations obtained are due in part to the differences in the free energies of formation of the chlorides of the elements involved, and in part to the differences in the free energies of alloying of the metals being separated in the metals at the two ends of the salt “bridge”.

In fuel reprocessing the stainless steel LMFBR cladding is removed by selective dissolution in molten zinc at about 800°C. The zinc-stainless steel alloy is separated from the solid mixed oxide fuel. The oxides are reduced to metals by reduction with calcium in a molten salt mixture of CaCl_2 - CaF_2 (as in the Thorium-Based Fuel Recycle process described below) in the presence of a Cu-Mg alloy. Uranium, plutonium, and the fission product rare earths yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, gadolinium and terbium, along with the fission products zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, cadmium, indium, tin and antimony dissolve in the alloy. Uranium is present in excess of its solubility and precipitates as UCu_5 . A fraction of the rare earths is transferred from the donor alloy to a Zn-Mg acceptor alloy by circulating a $\text{KCl-MgCl}_2\text{-CaCl}_2$ salt between the alloys. Radiation from the intentionally un-transferred rare earths provides proliferation resistance for the plutonium and

uranium with which they remain in the donor alloy. Uranium, plutonium and the remaining rare earths are separated from the other fission products by a second salt transfer process using a $\text{MgCl}_2\text{-MgF}_2$ salt. Zn-Mg is again the acceptor alloy.

The zinc and magnesium acceptor alloy elements are separated from the actinides by vacuum distillation and are recycled. The actinides along with those fission products that remain with the actinides are converted to oxides by reaction with oxygen for use in fuel fabrication. The primary process reactions are carried out in tungsten crucibles.

Equations (1) and (2) illustrate the roles of the formation of chlorides and of magnesium alloys in the separation of plutonium. Each metallic element from the fuel undergoes a similar set of reactions, but to differing degrees, thus providing the basis for the separations.

The donor reaction for plutonium is:



The acceptor reaction for plutonium is:



4.2.2 Electrorefining

The Electrometallurgical Process [303,304] is a relatively low-decontamination electrorefining process for separating uranium and plutonium from fission products to produce low-volume wastes. It employs molten alkali metal salts and molten cadmium and its alloys to separate actinides from fission products and other fuel materials. It produces metallic cladding wastes, chloride salt wastes that contain fission products, a zeolite waste that contains actinides and fission products, and uranium and plutonium streams. The waste stream of greatest concern is the zeolite, which may be combined with glass to produce a more conventional high-level waste form.

The electrometallurgical process was developed to recycle metallic fast reactor fuels such as the uranium-plutonium-zirconium alloy Integral Fast Reactor (IFR) fuel and the “fissium” alloy which comprised EBR-II fuel. The process is adaptable to oxidised uranium metal fuel or to oxide-based fuels such as LWR UO_2 by the addition of a head-end step that reduces the metal oxides to metals. It has been developed through large-scale engineering cold demonstrations and small-scale hot tests using plutonium as well as uranium.

The process is based upon differences in the redox potentials in molten salts of the actinides, fission products, cladding materials and materials of construction present in the process. It is also based on the fact that plutonium forms a stable intermetallic compound (PuCd_6) with molten cadmium whereas uranium does not, thus providing a Gibbs energy driving force for the selective reduction of plutonium into molten cadmium. Quantitative separation of the uranium from plutonium is achieved by potentiometrically controlled, preferential electrodeposition of the uranium on an iron cathode. These differences in behaviour are employed to selectively separate uranium and plutonium from the majority of the fission products and from each other and to produce a relatively low-volume, highly radioactive salt waste stream essentially free from actinides.

Salt and cadmium occluded with the uranium and plutonium respectively are separated by distilling them at high temperatures.

Fission products (most notably caesium and strontium) are separated from the salt by sorbing them on a zeolite so the salt may be re-used, although a side stream of the salt must be discarded periodically because of build-up of impurities such as sodium and heat-generating fission products.

The thermodynamic basis [305] and the chemical basis [306] for pyrochemical processes for use with metallic fuels have been discussed by workers in the field.

4.2.3 Dry processes

A large number of processes based on reactions between gases and solids have been proposed to recycle spent reactor fuels. Although these may have some applications to treating actinide wastes, they are primarily directed toward fuel recycle, and claim proliferation resistance as a major advantage. In general, the claimed proliferation resistance derives from incomplete removal of fission products. References to these processes are included here for the sake of completeness of information that may have application to separation of actinides in wastes: AIROX [307-309], DUPIC [310-312], RAHYD [313] and CARBOX [313].

In addition to the dry processes there have been several feasibility studies of fuel recycle processes based on the use of molten metals. These include the molten tin process [314], the DAP process [315], and a thorium-based fuel recycle process [316].

4.2.4 Volatilisation

Volatilisation of the actinides in various chemical states has proven to be a very useful process for their separation from each other and from impurities. Volatilisation is often highly selective, especially for uranium, but for other actinides as well. The fluorides in particular have found extensive use in separations. Actinide compounds with the other halides are much less selective. Americum metal has a usefully low volatilisation temperature.

4.2.4.1 Fluoride volatility

The search continues for alternative processes that may be cheaper than the PUREX process, for instance by avoiding the need to manage large volumes of liquid waste (see Section 4.1.6). One possibility that has been known for many years is to utilise the volatility of uranium hexafluoride to separate it from fission products and other impurities.

Fluoride volatility [317] is a generic term given to a large number of processes. There are a large number of hexafluorides [318], all of which have relatively high volatilities. The non-metallic hexafluorides are generally much more volatile than the metallic hexafluorides. In the context of actinide separations the term fluoride volatility is customarily used to designate the separation of uranium as the hexafluoride from a variety of other materials. The high volatility and chemical stability of uranium hexafluoride provide the basis for what is by far the most widely used pyrochemical process, namely selective formation and volatilisation of UF_6 to produce a very pure uranium-containing product suitable for use in isotope separation and in fuel preparation.

Uranium as an impure uranium ore concentrate or as a constituent of a molten salt such as has been used in the Molten Salt Reactor Experiment (MSRE) may be directly fluorinated [319] with fluorine gas to produce and separate the volatile hexafluoride. Impurities that also form volatile fluorides may be removed from the UF_6 by selectively sorbing them on solid sorbents such as NaF, CaF_2 , alumina and activated charcoal [320]. These sorbents then become wastes.

Uranium hexafluoride may also be produced from uranium tetrafluoride by reaction with oxygen to form UF_6 and UO_2F_2 , although this reaction has not found commercial application.

4.2.4.1.1 XeF_2 and KrF_2

XeF_2 has been used as a fluorinating agent of UO_2 in a fluidised bed reactor using Al_2O_3 as a diluent to absorb thermal shock. The fluorination rate was higher than for pure F_2 , although the same rate could have been attained with F_2 by increasing the reaction temperature by $150^\circ C$. The fluorination proceeds in two steps with the formation of UO_2F_2 as an intermediate compound that converts to UF_6 only at temperatures above $300^\circ C$. The UO_2 conversion achieved was typically about 60%. The chemical reaction rate was the rate controlling step in the reactor. XeF_2 can be formed by reaction of fluorine with xenon at high pressures. KrF_2 has been studied by Kim and Blum [321] for use as a fluorinating agent to recovering actinides from reprocessing plant incinerator ashes. It is assumed that fluorination could be carried out most conveniently in a fluidised using an inert carrier gas. Although fairly difficult to prepare, once made KrF_2 is more stable than FOOF (see Section 4.2.4.1.2).

4.2.4.1.2 Fluorperoxide (FOOF)

FOOF [322] is a fluorinating agent that shows promise for use in place of F_2 as a fluorinating agent. It may be used to produce actinide fluorides as well as to fluorinate surfaces to enhance their decontamination from actinides, most notably plutonium and uranium. It is, however, unstable and should be used within hours of its production.

4.2.4.2 Vaporisation of metals

Vaporisation of metals [323] has been used with some success in industrial applications, especially to produce vapour deposited metallic surfaces. Of the metallic actinides, only americium has a volatility high enough to be useful in a processing method. The vapour pressure of solid americium (given in atmospheres of Am) from 298 K to its melting point is given by the equation:

$$\log_{10} P_{\text{vap}} (\text{atm}) = 6.977 - \frac{14\,854}{T} + 0.1914 \log_{10} T - 4.699 \times 10^{-4} T$$

At temperatures above its melting point (1 450 to 1 820 K) and in dilute solution of americium ($<2 \times 10^{-5}$ mole fraction) in plutonium, the vapour pressure is given by:

$$\log_{10} P_{\text{vap}} (\text{atm}) = 4.14 - \frac{11\,300}{T}$$

4.2.4.3 Chloride volatility

Chloride volatility [324] is a considerably less selective process than fluoride volatility because of the much larger number of volatile chlorides than volatile fluorides. Consequently, less effort has been expended on their development. They do, however, hold the promise of greater flexibility than fluoride processes because of the greater solubility in water of most chlorides, which affords a ready link to aqueous processes.

In some large-scale separation processes, especially those involving recycle of plutonium in weapons, large amounts of alkali metal chloride salt wastes are produced that may contain up to 10% plutonium as plutonium chloride, plutonium oxychloride, plutonium oxide and plutonium metal. The alkali metal chlorides, typically a eutectic mixture of NaCl and KCl, can be separated from the plutonium by distilling them at about 850°C if the plutonium is first oxidised to non-volatile PuO₂ by the addition to the melt of a carbonate such as CaCO₃, which is soluble in the chloride melt. It has been established that kilogram quantities of alkali metal chloride salts can be distilled per day. However, distillation temperatures in excess of 1 200°C are needed to separate the CaCl₂ from the PuO₂. This imposes a rather severe requirement for special construction materials for the process equipment.

It is possible in principle to reduce the plutonium concentration in the alkali metal chlorides to 10⁻¹⁰ parts per million; however, in actual practice, equipment contamination limits the amount of separation to a much smaller value. Nonetheless, it appears to be possible to meet or exceed the 3.7 MBq/kg (= 100 nCi/g) criterion which defines TRU waste.

4.2.5 Miscellaneous

In addition to the actinide separation processes discussed above there are a number of relatively new and as yet not widely adopted separation processes. Some of these have found applications in non-nuclear areas, while others are unproven but may hold promise for use in actinide waste separations. Some of these processes are discussed below.

4.2.5.1 Quantum-CEP

The Quantum-CEP process [325] is a relatively new process for treating wastes by reacting them with molten metals, most commonly with iron. It is based on the fact that when wastes are added to molten iron at about 1 600°C they can react to produce gaseous products, reduced metals that dissolve in the iron, and a slag that contains non-volatile oxides of any metals more reactive with oxygen than iron is. Aluminosilicate and borosilicate vitreous slags have been used as host materials for the slag phase. Control of the system's oxygen over-pressure controls the degree to which any carbon dissolved in the iron reacts to form carbon monoxide gas, and thus controls the redox potential of the system. Also, injection of oxygen into the iron provides mixing that facilitates mass transfer. At very low carbon concentrations in the iron, iron oxide is formed in preference to carbon monoxide.

This process was developed to deal with organic wastes, for which it is exceptionally well suited. It has, however, been adapted for use with inorganic wastes including depleted uranium as UF₆. When carbonaceous materials such as ion exchange resins or any of a variety of hydrocarbons that may contain actinides are added to the system they are completely decomposed, typically producing a gas phase consisting of a mixture of water and carbon monoxide (synthesis gas). Resins containing

only hydrogen, carbon and nitrogen are converted to gases (nitrogen is evolved as nitrogen gas). If phosphorus, sulphur or chlorine are present they may be either evolved as gaseous compounds or contained in the slag, depending on additives to the slag. Conditions may be selected that will produce HCl gas from chlorinated hydrocarbons.

4.2.5.2 Melt refining

Melt refining [326] is the name given to the process of selective removal of fission products from irradiated metallic fuel by high temperature oxidation in which an oxide ceramic crucible is the source of oxygen. Volatilisation of some fission products contributes to their overall removal.

This process is primarily of historical interest with regard to its initial application to metallic EBR-II fuel.

4.2.5.3 GMODS

The GMODS process [327, 328] is a method proposed for the direct, single step conversion of plutonium-containing materials to glass. Plutonium-containing materials are fed to molten lead borate glass which reacts to produce metallic lead and oxides of the plutonium-containing materials. The oxides dissolve in the lead borate glass to produce a mixture which floats on the molten lead. Boron oxide in the glass aids the rapid dissolution of metal oxides into the molten glass. Any organic materials present are oxidised to oxides of carbon and to steam. Glass frit and carbon are added to adjust the composition of the glass and to reduce any excess lead oxide to metallic lead. After removal of the product glass from the melter, boron and lead oxide are added to the melter to replace materials that have gone into the glass. The metallic lead is re-oxidised to lead oxide by addition of oxygen.

4.3 Processes based on fields

Techniques using force fields to perform separations have found limited application on anything other than a laboratory scale outside the pharmaceutical industry. Nonetheless, they hold promise for some applications in waste stream treatment for actinide separations [329].

4.3.1 Electrical fields

Electrokinetic phenomena have been commercialised for removal of heavy metals from soils and ground water in the Netherlands [330], the UK [331] and the US [332]. The “Lasagna” process [333] in particular has been used to clean up uranium-polluted soils.

Another quite different use of electricity in separations is in a new device called the emulsion-phase contactor (EPC), which is used to greatly enhance solvent extraction efficiency, while reducing stage heights as much as two orders of magnitude. In the EPC electric fields are used to form nearly mono-disperse droplets of one liquid phase in another and subsequently to coalesce them. A pilot EPC has operated at specific throughput rates over 40.74 l/m²·min (1 gal. per square foot per minute).

Field-stabilised filtration beds may be used to achieve very high throughput while achieving good separations, but have not yet found many applications.

4.3.2 Centrifugal fields

Centrifugal fields have found wide application in separations of solutions of high molecular weight organic materials, especially of biologically important species. They have not found practical applications in relatively simple, inorganic systems, although there is no fundamental reason while they might not be used for such systems. Recent advances in materials of construction of centrifuges have made possible generation of the very large centrifugal force fields that would be necessary to separate simple actinide compounds or elements. Although no practical demonstration of such separations has been carried out, theoretical considerations suggest that in simple, well behaved liquid systems such separations should be possible.

It is possible in principle to separate actinides from fission products in liquid solutions by centrifugation. In the ideal case it is only required to overcome the entropy of mixing. In actual practice it is likely that there will be energy of interactions of the species comprising the solution which must also be overcome. Bowman [334] examines the possibility of a two-step process for separating actinides from fission products in a molten salt solvent mixture of LiF and BeF₂. The first step is to remove the bulk of the molten salt solvent by centrifugation. In the second step the fission products contained in a small fraction of the molten salt solvent are separated from the bulk of the actinides by centrifugation. Bowman concludes that such a separation should be possible with practical centrifuge rotational speeds and available materials of construction.

4.3.3 Magnetic fields

High magnetic gradient separators (HMGS) have been used in special waste stream treatment applications where a bulk ferromagnetic or paramagnetic material is to be separated from a high-volume flowing stream [335], but have not found wide application specifically to actinide separations. However, selective extractant materials have recently been formed on ferromagnetic particles to permit their removal from a complex mixture by HMGS and subsequent treatment to elute the sorbed actinide or other radionuclide [336]. In addition, actinide separations by ion exchangers coated on magnetic particle substrates or by carrier precipitation on materials such as magnetite and MnO₂ which may subsequently be separated magnetically may find application. Kochen and Navratil [337] report on the use of ferrites (activated magnetite) attached to resin beads for the removal of actinides from alkaline aqueous solutions. They determine that the use of an externally applied magnetic field significantly enhances actinide removal. Tsouris and Yiacoumi [338] study the flocculation and filtration of paramagnetic particles using high-gradient magnetic fields, and Yiacoumi *et al.* [339] examine the mechanism of particle flocculation by magnetic seeding.

4.4 Relationship of kinetics to separations

It is possible that separations could be based on rate-controlled processes if greater knowledge of some kinds of rate data were available. An example of this could be in solvent extraction processes where the rate of extraction of one actinide species could be so much larger than that of other species that it could be extracted before the others, even though the equilibrium separations did not permit as good a separation. In principle the rates of separations may be controlled either by chemical or physical processes. The slow extraction and stripping of Fe(III) was discussed (Section 4.1.1.4) in connection with its separation from actinides and lanthanides in the DIAMEX process.

4.4.1 Chemical control

Chemically controlled rates of reactions in solution often involve the slow removal or addition of oxygen contained in oxygenated ions such as MO_2^{2+} , where M may be U, Np, Pu, or Am. Reactions involving only the removal or addition of electrons to an ion may be expected to be rapid, and would probably not afford a basis for rate-dependent separations. Plutonium in particular undergoes kinetically slow hydrolysis reactions in both the tetra- and hexavalent states [37].

Although practical use of such reactions has yet to be made, there is reason to believe that with the rapid phase separations now available with centrifugal contactors and the rapid exchange rates in macroporous resins, as well as other rapid methods for separating phases, they may eventually prove to be feasible.

4.4.2 Diffusion control

In many separation processes the rate is controlled by the rates of diffusion of ions into pores and across interfaces. This is particularly true of separations involving liquids, e.g. solvent extraction and ion exchange, but it also applies to most processes involving two bulk phases. Slow rates of diffusion through ceramic membranes have been a major deterrent to their wider use in separation processes, and although they now show promise for salt splitting, ceramic membranes for actinides separations have yet to be devised. Organic ion exchange membranes are also somewhat limited by slow diffusion rates. In such cases a variety of complex phenomena come into play. These include hydrophobicity, electrical charge repulsion, and in some cases, ionic size.

Anything that can be done to alter the relative diffusion rates of actinides might be made the basis for their separation.

Section 5

DISCUSSION

5.1 Basic chemistry research needs

Although there has been a very large amount of basic research carried out on the actinide elements, starting even before the discovery of nuclear fission, the ever-increasing demands placed on the separation chemist have pushed the need for additional and different kinds of chemical understanding of the actinides beyond what is presently known. Many of the areas where information is still needed are discussed below.

5.1.1 Rate data

There is a dearth of data on the rate-controlling factors that may affect actinide separations. The rates can be those associated with oxidation and reduction, with association and dissociation of ligands, with diffusion across liquid and solid interfaces and with diffusion within solids and liquids. In some cases, for example in the case of reactions of plutonium oxide or polymer, the controlling rate is disaggregation or dissolution. Although some rate data exist, rates are very seldom known under actual process conditions, which can differ greatly from the idealised case.

5.1.1.1 Redox reactions

Some of the most important actinide separations are based on redox reactions. For example, the PUREX process is based on the different extraction behaviours of Pu(III) and Pu(IV) (see Section 4.1.1.1). Although a large number of basic studies have been made on the redox behaviour of the actinides, there is much less information available under actual process conditions. More importantly, the largest volume of actinide wastes (with the exception of spent fuel) is contained in alkaline media, where little is known about the redox behaviour of the actinides as it applies to separation processes. The actinides are in alkaline media in the presence of a large number of other chemical elements, many of which have multiple valence states and are capable of reacting with the actinides. It is important to know more about what will happen in these extremely complex systems when separation processes are carried out. In many cases it is possible to change the redox potential of an actinide by complexing it or binding it to an ion exchange site. If the change achieved is large enough, it may be separable from another species that would otherwise not be separable. Thus, there is a need for much more research in this area. Shilov *et al.* have studied the redox reactions of neptunium, plutonium, and americium in alkaline media [340] using a wide range of those oxidants commonly used in radiochemical processing. Rates of oxidation of Np(IV) and Pu(IV) were observed to increase with increasing alkali concentration and with temperature. Heating in the presence of reducing agents such as hydroxylamine, sulphite reduced the pentavalent actinides.

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5.1.1.2 Phase equilibria

Most separations are carried out under conditions approximating thermodynamic equilibrium. For molten salt systems the temperatures are usually high enough that equilibrium is attained very quickly, and thermodynamic factors rather than kinetic factors are of overriding importance.

For separations to take place it is necessary to move actinides selectively from one phase to another. Although a great deal of information exists about the equilibria of actinides between the more common liquid organic extractants and aqueous phases, promising new extractants are being developed all the time. Furthermore, phase equilibria data are needed under actual process conditions. The same situation exists for a very broad spectrum of equilibria in molten salt systems and for solid-liquid equilibria. New organic and inorganic ion exchange materials are being developed in a large variety of chemical compositions and physical forms that range from beads to tubes to sheets. In the latter case the sheets may be homogeneous or contain processing particles held in supporting matrices. The need for additional research on separations involving equilibria among phases will always exist, and research in this area promises to lead to more efficient and cost effective processes for actinide separations.

5.2 Inherent limitations on separation processes

There are inherent limitations, both fundamental (theoretical) and practical, on the degree of separation that may be achieved in any separation processes.

5.2.1 Fundamental

In general, the theoretical limitations on separations derive from thermodynamic properties of the species whose separation is sought. For example, it is not practical to separate two actinides or an actinide from a non-actinide element if the Gibbs energy changes for the respective separation reactions are too similar. There will be an overlap in the separations, as may be seen by plotting the equilibrium concentrations of the species to be separated as a function of their respective concentrations. Sometimes separations may be achieved despite these similarities by capitalising on differences in redox behaviour or in complexation.

5.2.2 State of the art

In addition to the fundamental limitations to achievable separations there are practical limitations that derive from the nature of the reagents used in separation processes and the behaviour of the equipment used. For example, in the case of solvent extraction it is not possible to achieve complete phase separation under actual process conditions. Droplets of one phase remain in the other phase, or reagent (solvent) degradation occurs and forms secondary materials that have very different extraction behaviour from the primary reagent. An example of this type of reaction might be the formation of dibutyl- and monobutylphosphate ion in the PUREX process.

Separation equipment, by its nature, has surfaces to which separation reagents may adhere and diminish the degree of separation achieved. Corrosion occurs and introduces small but sometimes significant amounts of chemicals into the process stream. Some of these materials may react in an adverse way, others may catalyse reactions. In some cases the energy imparted to the process by the action of the equipment may cause untoward reactions.

Section 6

PRIORITISATION

6.1 Bases for R&D prioritisation

There are several aspects of the actinide waste management problem which must be considered in deciding the priority given to waste stream treatment research and development (R&D). These include:

- (1) the mass or volume of the waste;
- (2) the concentration of the actinides in the wastes;
- (3) the expected difficulty of treating the wastes;
- (4) the short-term hazard presented by the waste;
- (5) the long-term hazard presented by the waste;
- (6) the projected cost of treatment;
- (7) the amount of secondary waste produced.

These issues are discussed below.

6.1.1 Mass/volume of waste

There is a very broad spectrum of waste types that contain actinides. By far the most important separation problems are those involving the volume of waste that is stored in waste tanks as a result of fuel reprocessing, either in connection with national production of weapons plutonium or with commercial fuel reprocessing. This type of waste also contains the most radioactivity, although not necessarily the most actinides. It also poses the greatest technical challenge for treatment. Consequently, there is some merit in deferring treatment of this type of waste whenever possible in order first to gain a base of experience with less difficult to treat wastes. Putting off treating some of these wastes makes time available both for gaining practical experience in managing actinide wastes in general and in performing R&D necessary to deal with this most challenging type of waste. Thus, the priority given to treating high-volume actinide wastes should probably be intermediate; R&D should be at a moderate level, but adequate and steady. (An important exception is those tank wastes that pose safety issues.)

6.1.2 Actinide concentration

Actinide concentration in the wastes is another important aspect of the wastes that must be considered. If present in high concentrations, actinides produce heat and radiolytic effects in wastes and therefore early removal of them from some types of waste offers advantages with regard to convenience of storage and safety. Higher priority should be given to R&D for wastes with high actinide concentrations than that for those with low actinide concentrations.

6.1.3 Expected difficulty

Some types of waste are in a form or location that makes their treatment exceptionally difficult. There is merit in considering deferring their treatment until other types of actinide-containing wastes are treated. This allows more rapid progress to be made in managing the overall waste problem, and provides time for a base of experience to be built for treating these more difficult to treat wastes. However, because of the difficulties, the priority given to R&D for treatment of these wastes should be relatively high and closely tied to the experience base gained in managing more easily treated wastes.

6.1.4 Potential short-term hazard

If actinide wastes pose a short-term hazard, either real or potential, there is no choice but to proceed with their immediate treatment. This implies that the top priority for R&D be given to this type of waste. Wastes of this type might include, for example, those which are in the environment and moving toward the water table or are liable to be contacted by people either directly or by some transport mechanism. It also includes those which have the potential to explode because of production of explosive gases or excessive heat production.

6.1.5 Potential long-term hazard

Actinide wastes that pose a potential long-term hazard fall into a category that allows them to be treated either in the immediate or the distant future, depending on which of the other waste categories they fall into. In any event, the R&D priority assigned to this type of waste should be correlated with the short-term hazard of the wastes and related to the nature of that hazard.

6.1.6 Projected cost

Cost is a major factor in deciding R&D priorities for waste treatment. Although cost should not be allowed to defer treatment of wastes that pose an imminent hazard, it can be the deciding factor in all other categories being considered. However, care must be taken to consider all costs when making the determination of what to do first. In some cases reducing costs in the short-term can greatly increase the total cost of waste management when all the costs involved are properly taken into account. Thus, setting the R&D priorities on all the above waste types must be considered in the context of overall cost – what are sometimes called “life cycle costs”.

6.1.7 Secondary wastes

Finally, it is important to consider how much additional, or secondary, waste is produced when wastes are treated. If R&D can substantially reduce the net volume of waste, then it may be very cost effective to do that R&D early rather than later. A determination of this type requires that a great deal be known about the waste treatment processes to be used. Most often this level of information detail is not known or known only imperfectly. Nonetheless, it is important to make an attempt to establish bounding limits within which R&D priorities may be established.

Section 7

RECOMMENDATIONS

7.1 Basic chemical data

Despite the long history of work on actinide separation, there is a continuing need for basic chemical data as the emphasis shifts from separating plutonium for use in weapons, or plutonium and uranium for the nuclear fuel cycle, to cleaning up wastes and restricting environmental contamination. This is especially true because of the very large volumes of wastes in a wide variety of liquid and solid matrices and the low to extremely low concentrations of actinides in the wastes and the environment. It is especially important to promote and maintain support in molecular modelling. A great deal of time and money can be saved by modelling both actinides and separation reagents and their interactions. Therefore, it is recommended that work be continued on the elucidation of chemical properties of the actinides, especially in the conditions under which they exist in managed wastes and in the environment. Recognition of this need is evidenced in the US by the recent establishment within the US DOE of a new initiative in basic science in support of its environmental management programme.

7.1.1 Chemical thermodynamics

Measurements of equilibrium constants as a function of ionic strength and temperature are needed for the optimisation of separations. In addition solubility product and redox potential measurements are needed. The thermodynamic (phase equilibrium) behaviour of the more complex chemical systems found in managed wastes and in the environment need to be understood if efficient and economical processes are to be developed. It is recommended that there be support of work on thermodynamics of systems of practical importance.

7.1.2 Chemical kinetics

There is a lack of information on the rates at which some chemical processes of significant practical importance occur. This is especially true of reactions that involve changes in valence state between oxygenated and un-oxygenated states and that involve reaction with large molecules such as those found in the natural environment. It is recommended that special attention be given to the kinetics of solvent extraction, and to development of reactant materials that react rapidly either by enhancement of mass transfer or by enhanced rates of chemical reaction. It is possible that separation could be based on differences in reaction rates of species whose separation is sought rather than on their equilibrium states.

7.1.3 Extraction chemistry

Preferential extraction of one species over another is the basis of some the most important actinide separations. New reagents and separation media are constantly being developed, and new waste matrices are coming to the fore as needing treatment. Because extraction is so important there is a continuing need for basic understanding of the selectivity shown by extraction systems that may find application to separation problems that are at present intractable or not practicable for reasons of cost or technical difficulty. Therefore, it is recommended that work be carried out on acquiring the basic knowledge required to discover and to support new and promising extraction techniques and reagents.

7.1.4 Separations based on force fields

There has been only a very modest amount of work on separations based on such things as electrical, magnetic or centrifugal force fields. It is conceivable that in specialised applications separations based on such fields will be the method of choice. It is recommended that work be conducted on advanced separation methods with special emphasis on those basic data that will be most supportive of solving practical waste and environmental problems.

7.1.5 Analyses related to separations

There is an ever present need for improved and new analytical techniques. There is a special need for *in situ* analytical techniques that do not involve the risks and expense of taking and transporting samples. Furthermore, as regulations governing waste management and environmental clean-up grow more demanding, requiring more precise and accurate measurements of actinides at lower and lower concentrations, novel approaches are needed. It is recommended that work be carried out on development of novel, cost effective and more sensitive analytical techniques and equipment.

7.1.6 Speciation; activity coefficients; solvolysis

A fundamental understanding of the interrelations of speciation, activity coefficients and solvent interactions is required if better and more subtle separations are to be achieved. This is true both of aqueous and non-aqueous systems. In non-aqueous systems in particular, activity coefficients are likely to be either much larger or much smaller than those found in aqueous media, and to have a profound effect on the separations. Intermetallic compounds are also of great importance in systems such as those found in pyrometallurgical processes. In this case the major metallic component, e.g. molten cadmium, may form an intermetallic compound with a metal such as plutonium or uranium with a large Gibbs energy and thereby totally alter the equilibrium from that which might otherwise have been expected.

7.2 Separation chemistry

7.2.1 Hydrometallurgy

As new and more selective extractants and precipitants are developed to meet the ever more demanding needs for separating actinides, they should be carried through small-scale engineering development to establish their practical utility. Those that survive laboratory screening should

be tested on real wastes on a meaningful scale. It is recommended that work continue at this level of development and demonstration to find those processes that solve important and pressing actinide separations problems to drive down the costs and hasten the process of clean-up.

7.2.2 Pyrochemical processes

For certain types of wastes pyrochemical processes will be the actinide separation process of choice. Pyrochemical processes are demanding both from the point of view of operating conditions usually required and because of challenges to materials of construction. For this reason it is important to maintain interest and support for the chemistry and electrochemistry of actinides in molten salt systems. In general, pyrochemical processes require a fairly long lead time to establish their feasibility. It is recommended that work be carried out at a level that ensures an understanding of the practical problems they entail, and that ensures that they are available for use on those problems that are best treated by them.

7.2.3 Processes based on force fields

Although electrical, magnetic and centrifugal fields have been used rather widely in industrial applications, they have found very little use in radioactive waste stream and environmental clean-up. There have been a few studies on the use of electroosmosis to move radioactively contaminated groundwater in an attempt to facilitate its clean-up, but these applications have been few in number. It is clear that there are some clean-up problems for which force fields are applicable and the small amount of work done to date has been encouraging. It is recommended that non-nuclear industrial applications be scrutinised for applicability to radioactive waste problems, and that they be studied, where appropriate, to see if they are applicable and advantageous for use with radioactive wastes.

7.2.4 Kinetics of separations

Chemical separations involve the distribution of a material between two phases. That distribution is very often rate-limited. The limiting factor may be either physical or chemical. In solvent extraction and ion exchange the separation rate is very often limited by the rate of diffusion of a species across an interface or into a bulk phase. In some cases the rate limiting step is chemical in nature, and may involve a redox reaction or a slow association or dissociation of the species being separated and a ligand. Because these rate-limiting steps are often species-dependent, opportunity may exist to capitalise on differences in the rates of different species to participate in the separation, even though the equilibrium states of the species may be essentially the same. Use of this property of a system may make possible a relatively easy separation where none was available by other means. Very little effort has been spent on this promising approach, and it is recommended that special attention be given to support of studies in this area.

Section 8

CONCLUSIONS

As described in Chapters 2, 3 and 4, a great deal of basic research has been carried out on actinide separation chemistry, from fundamental studies to applications. However, there are many areas where information is still needed for additional and different kinds of chemical understanding of the actinides beyond what is presently known. It should be pointed out that although a large number of basic studies have been made on chemical reactions of the actinides, less information is available under actual process conditions e.g. high ionic strength, the presence of a large number of other chemical elements and multiple valence states of actinides. In addition inherent limitations on separation processes exist. One example is the difficulty of complete phase separation; another is the effect of degradation products or impurities produced by corrosion of the equipment material.

There are several aspects of the actinide waste management problem which must be considered in deciding the priority given to waste stream treatment research and development (R&D). The Task Force established the following priorities:

- If actinide wastes pose a short-term hazard e.g. by contaminating the environment or by increasing an explosion hazard, there is no choice but to proceed with their immediate treatment. This implies that the top priority for R&D be given to this type of waste.
- If present in high concentrations, actinides produce heat and radiolytic effects in wastes and therefore early removal of them from some types of waste offers some advantages with regard to convenience of storage and safety. Higher priority should be given to R&D for wastes with high actinide concentrations than for those with low actinide concentrations.
- There is some merit in deferring treatment of high-volume waste whenever possible in order to first gain a base of experience with less difficult to treat wastes. Thus, the priority given to treating the high-volume actinide wastes should probably be intermediate; R&D should be at a moderate level, but adequate and steady.
- If R&D can substantially reduce the net volume of waste, then it may be very cost effective to do that R&D early rather than later. A determination of this type requires that a great deal be known about the waste treatment processes. Most often this level of information detail is not known or known only imperfectly. Nonetheless, it is important to make an attempt to establish bounding limits within which R&D priorities may be established.
- Actinide wastes that pose a potential long-term hazard fall into a category that allows them to be treated either in the immediate or the distant future, depending on which of the other waste categories they fall into. In any event, the R&D priority assigned to this type of waste should be correlated with the short-term hazard of the wastes and related to the nature of that hazard.

- From the view point of overall waste management, there is merit in considering deferring treatment of some types of waste which are exceptionally difficult to deal with until other types of actinide-containing wastes are treated. However, because of the difficulties, the priority given to R&D for treating these wastes should be relatively high and closely tied to the experience base gained in managing more easily treated wastes.
- Care must be taken to consider all costs when making the determination of what to do first. Setting the R&D priorities on all the above waste types must be considered in the context of overall cost – what are sometimes called “life cycle costs”.

Finally, the Task Force made recommendations using a 25 year horizon for the needs as a practical extension of the R&D on actinide separation chemistry in the future. With regard to basic chemical data, it is especially important to promote and to maintain support for molecular modelling. A great deal of time and money can be saved by modelling both actinides and separation reagents and their interactions. Measurement of thermodynamic constants in more complex chemical systems are recommended for the optimisation of separations. Special attention should be given to the kinetics of solvent extraction, and to development of reactant materials that react rapidly either by enhancement of mass transfer or by enhanced rates of chemical reaction. Work should be carried out on acquiring the basic knowledge required to discover and to support new and promising extraction techniques and reagents. Work should be conducted on separations based on force fields with special emphasis on those basic data that will be most supportive of solving practical waste and environmental problems. It is recommended that non-nuclear industrial applications of force fields be scrutinised for applicability to radioactive waste problems. For analyses related to separations, development of novel, cost effective and more sensitive analytical techniques and equipment is necessary.

From the view point of separation chemistry, it is recommended that development and demonstration of those hydrometallurgical processes that solve important and pressing actinide separations problems be conducted to drive down the costs and hasten the process of clean-up. Pyrochemical processes have a place in actinide separation processes, and work should be carried out at a level that ensures an understanding of the practical problems they entail, and that they are available for use on those problems that are best treated by them.

The Task Force of the NEA/NSC hopes that this report will be useful to the community of chemists and chemical engineers in charge of the definition of new treatments of actinide bearing wastes, which are certainly among the most important issues which will be addressed in the future within the nuclear industry.

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